15136

ACCELERATED RADIATION POLYMERIZATION OF VINYL-DIVINYL COMONOMER SYSTEMS

by

MICHAEL M. MICKO

B.Chem (Eng.), Slovak Technical University, Bratislava, 1959

C.Sc. Slovak Technical University, Bratislava, 1966

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department

of

Forestry

We accept this thesis as confirming to the required standard.

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1973

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Forestry

The University of British Columbia
Vancouver 8, Canada

Date May 10/73

ABSTRACT

Gel-effect (Ge) acceleration in radiation polymerization of methyl methacrylate (MMA)-divinyl monomer (DVM) systems and properties of resulting polymer products have been investigated. Four methacrylate esters with variable molecular bridge length between the double bonds, i.e., ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA) and tetraethylene glycol dimethacrylate (TEGDMA), were used as DVM accelerators and crosslinking agents.

The course of polymerization was followed by temperature (T)-time(t) polymerization exotherm curves. A new technique was developed to determine the "Gel-Effect Point" (GEP) and individual polymerization parameters associated with gelation in crosslinked network, i.e., polymerization rate coefficient (PRC), curing time (t_{MAX}), overall curing rate ($1/t_{MAX}$), and overall acceleration constant (K).

The overall curing rate was found to be proportional to the volume concentration of crosslinking agent only up to 15 to 20% DVM in the system. Within this concentration interval

the overall acceleration constants increased with molecular distance between DVM double bonds in the following order: EGDMA (1.1×10^{-3}), DEGDMA (1.5×10^{-3}), TrEGDMA (1.8×10^{-3}), and TEGDMA (2.4×10^{-3} min^{-1} $conc.^{-1}$). Half-time concentration values, i.e., concentration of divinyl monomer required to reduce the curing time to one-half of that for pure MMA, increased in reverse order. Numerically, half-time concentration values for TEGDMA, TrEGDMA, DEGDMA, and EGDMA were 3, 4, 5, and 7% respectively.

The calculated overall acceleration constant allowed prediction and calculation of curing times for individual comonomer mixtures. The agreement between predicted and experimentally measured values was within 5% error. The derived empirical equation for prediction of curing time was also applicable to the heat-catalyst polymerization system.

All divinyl monomers studied were found to be efficient crosslinking agents and improved the thermomechanical and strength properties of the resulting copolymers. The compression stress, strain and toughness exhibited well defined maxima within 5-10% of divinyl monomer in the mixture. Within this concentration interval both maximal acceleration and superior mechanical properties of copolymers were obtained. The numerical value of copolymer connection number (CN_{co}) was found to be a useful structural parameter relating mechanical and thermomechanical properties with copolymer crosslinking density.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

FIGURE PAGE

LIST OF SYMBOLS

a	=	Number of 2-way connected atoms
AMA	=	Allyl methacrylate
AN	=	Acrylonitrile
b	=	Number of 3-way connected atoms
BMA	=	Butyl methacrylate
c	=	Number of 4-way connected atoms
CN	=	Connection number
CN_{co}	=	Copolymer connection number
d	=	Specific gravity, g/cm^3
D	=	Radiation dose, Mrad
dp	=	Depth of penetration, mm
DP	=	Degree of polymerization
DVB	=	Divinyl benzene
DVM	=	Divinyl monomer
DEGDMA	=	Diethylene glycol dimethacrylate
E	=	Modulus of elasticity, kg/cm^2
EGDMA	=	Ethylene glycol dimethacrylate
f	=	Monomer functionality
F	=	Area under the stress-strain curve, cm^2
Ge	=	Gel-effect
GEP	=	"Gel-Effect Point"
h	=	Polymer sample height, mm
k	=	Sensitivity constant, mils/inch
K	=	Overall acceleration constant, min^{-1}. $conc^{-1}$
k_p	=	Propagation rate constant
k_t	=	Termination rate constant
LTDC	=	Linear thermomechanical deformation coefficient, $1/^oC$
M	=	Monomer
MAX	=	Exotherm maximum, "Cure"
mf	=	Mole fraction
MMA	=	Methyl methacrylate
MW	=	Molecular weight
n	=	Number of $-O-CH_2-CH_2-$ units in DVM
OAC	=	Overall acceleration constant
OCR	=	Overall curing rate
OGR	=	Overall gelation rate
p	=	Extent of polycondensation reaction, %
P	=	Dead polymer
PPC	=	Paper polymer composites
PRC	=	Polymerization rate coefficient, $^oC/min$
PRCI	=	PRC in "Activation" period, $^oC/min$
PRCII	=	PRC in "Acceleration" period, $^oC/min$
poly(MMA)	=	Poly(methyl methacrylate)
poly(S)	=	Polystyrene

$R^{\bullet}$	=	Primary radical
Ri	=	Rate of initiation
$RM^{\bullet}$	=	Growing polymer radical
Rp	=	Overall rate of polymerization, %/hr
s	=	Slope of thermomechanical curve in transition region
S	=	Styrene
t	=	Time, min
T	=	Temperature, ^{o}C
TBS	=	t-Butyl styrene
TDD	=	Thermal deformation degree, %
TDT	=	Thermal distortion temperature, ^{o}C
TEGDMA	=	Tetraethylene glycol dimethacrylate
T_g	=	Glass transition temperature, ^{o}C
t_{GEP}	=	Time to onset GEP, min
T_{GEP}	=	Temperature at GEP, ^{o}C
t_{MAX}	=	Time to reach exotherm maximum, min
T_{MAX}	=	Temperature at exotherm maximum, ^{o}C
TMPTA	=	Trimethylol propane triacrylate
TMPTMA	=	Trimethylol propane trimethacrylate
TrEGDMA	=	Triethylene glycol dimethacrylate
VA	=	Vinyl acetate
VAD	=	Vinyl adipate
VC	=	Vinyl chloride
VPC	=	Veneer polymer composites
VS	=	Vinyl succinate
WPC	=	Wood polymer composites
I	=	"Activation" period
II	=	"Acceleration" period
η_{rel}	=	Relative viscosity

ACKNOWLEDGEMENTS

I wish to acknowledge contributions of all my present and previous teachers.

It has been my privilege to have been closely associated with Dr. L. Paszner, Research Associate, Faculty of Forestry and Dr. J. W. Wilson, Professor, Faculty of Forestry. I wish to express my thanks to both of them for valuable advice, constructive criticism, thoughtful considerations and helpful suggestions during the investigations and preparation of this dissertation. Their support provided over the past years is deeply appreciated.

I wish to thank the University of British Columbia for Graduate Fellowships; the Faculty of Forestry for Research Fellowships and other financial support; Dr. R. W. Wellwood and Dr. N. C. Franz for support from an NRC operating grant during final stages of thesis preparation.

Appreciation is also expressed to Miss E. Budyk and technical staff; in particular, to Mr. U. Rumma and G. Bohnenkamp for help with construction and calibration of the thermomechanical analyzer.

Last but not least, I am grateful to my wife Gitka and children Michelle and Martin-Mike for their great patience and sacrifice over the many weekends devoted to this study and its reporting.

INTRODUCTION

Wood is a valuable material, used traditionally in its natural state. Ease of fabrication and finishing, pleasing appearance, high strength to weight ratio and low cost are characteristics contributing to its wide use.

Numerous attempts have been made to improve inherent wood properties. Finishes have been developed to increase resistance to weathering and mechanical abrasion, treatments have been developed to improve dimensional stability or to impart greater resistance to decay, fire and biodegradation. One treatment of current interest is the combination of wood with polymers to form wood polymer composites (WPC).

A means for producing WPC involves impregnation and *in situ* polymerization of vinyl monomers in wood structures. Among techniques available for curing WPC, radiolytic polymerization has been much examined (4,5,30,31,49,54,55,56, 82,84,85,90,93,99). After a decade of extensive experimentation and development, WPC products have begun to appear in the market (30). Monomers such as methyl methacrylate (MMA) and styrene (S) are economically attractive.

A major restriction imposed by most monomers employed in WPC manufacture has been long curing schedules, and

corresponding high dosages required to complete radiolytic polymerization. The requirement with S, as example, is not only beyond reasonable economics, but so large as to degrade the wood substrate. Certainly, better radiation efficiency has become a necessity to further process development.

Several methods have been used to accelerate radiation polymerization of vinyl monomers incorporated in wood matrices. Addition of low molecular weight compounds, particularly carbon tetrachloride (CCl_4), was found to accelerate the radiation curing of various vinyl monomers (30,55,90,93). However, secondary effects caused by CCl_4, particularly by its function as a chain-transfer agent (22), are so disadvantageous that it is not considered for technological applications (30,82).

It has been known from the theory of monomer gelation (38) that incorporation of small amounts of crosslinking agents, containing two or more vinyl groups, allows formation of three-dimensional networks which, during early stages of polymerization reactions would turn the comonomer system into a gel. Relatively little work has been done to utilize the phenomena of gelation to accelerate radiation polymerization. So far only Raff et al. (84) and Kent et al. (55) have paid limited attention to acceleration in vinyl-divinyl comonomer systems as related to radiation processing of WPC. Recently, during quite

advanced stages of this work, Kenaga (53) and Duran and Meyer (33) attempted to utilize this method in randomly chosen heat-catalyst systems.

A systematic study of gelation kinetics in vinyl-divinyl comonomer systems is completely lacking. Up to this point no quantitative information has been available on the following parameters:

i. differences in curing rates before and after the Gel-Effect Point (GEP),
ii. the temperature profile during polymerization,
iii. efficiency of different crosslinking agents,
iv. the influence of molecular bridge length between double bonds of divinyl monomer on regulating the propagation and termination reactions in gelled network, and
v. the relation between overall curing rate (OCR) and composition of comonomer mixtures.

The primary objective of the present study was to test the hypothesis that radiation polymerization of vinyl-divinyl comonomer systems may be accelerated by forming gelled three-dimensional networks. Further, characteristics of these networks should depend on divinyl monomer (DVM) features, such as bridge length between the double bonds. This should allow predictions of the polymerization course

and OCR by merely considering the DVM chemical structure. Since the hypothesis involves regulation of individual elementary steps of polymerization reactions it is expected that such findings would be fully applicable to acceleration of heat-catalyst systems.

Further purposes of this work were to:

i. develop techniques which allow monitoring of radiation polymerization to complete conversion, determination of GEP and associated parameters,

ii. investigate acceleration polymerization across wide ranges of comonomer concentration with various systems, and

iii. elucidate properties of various polymer products available from the systems examined and attempt to relate these to monomer structural features.

MMA was selected as the basic monomer for the study because of its present utility in WPC products and because of wide literature available on such composites. Another reason was compatibility of MMA with a commercially available homologous DVM series of glycol dimethacrylate esters.

The DVM crosslinking agents were ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA)

and tetraethylene glycol dimethacrylate (TEGDMA). To the best of the author's knowledge no literature relates molecular bridge length with gelation or acceleration in vinyl-divinyl comonomer systems.

The source of radiation was gamma rays from decaying ^{60}Co. It was chosen on the basis of its availability, proven effectiveness in initiation of MMA polymerization and its high penetrating power, normally required for large sections of wood composite products.

2.0 LITERATURE REVIEW

2.1 Radical Chain-Growth Polymerization

Polymers of the type important to this study are macromolecules built up by the linking together of a large number of unsaturated molecules termed monomers. Radical chain-growth polymerization is initiated by reactive species containing unpaired electrons, i.e., free radicals.

2.1.1 Free radicals; formation and reactions

Organic molecules containing one or more unpaired electrons are termed free radicals. They can be either monoatomic species or polyatomic aggregates of different chemical structure. Free radicals are generally considered to be highly unstable species because of their very short lifetime in reaction systems, particularly in homogeneous liquid or gaseous reaction media.

Production of free radicals may be accomplished by either of two general reactions:

i. homolytic decomposition of covalent bonds, or
ii. generation by an electron transfer mechanism.

Homolytic decomposition of covalent bonds into two

or more radical fragments may be accomplished by absorption of energy in almost any form; thermal, electromagnetic, electrical, sonic or mechanical. All these energy forms have been used for free radical production and initiation of radical chain-growth polymerization (22,36,59,60,78,106). For practical applications thermal and electromagnetic energy are the most important means by which free radicals are produced. The latter generally includes either of two major sources, ultraviolet light or high energy radiation. These are termed ionizing radiation.

Free radicals take part in a variety of destructive chemical reactions, such as oxidation and thermal degradation. The most important synthetic type reactions involving free radicals are:

i. addition to multiple covalent bonds, and
ii. radical termination reactions.

Both reactions are crucial to radical chain-growth polymerization with vinyl monomers and will be discussed later in relation to specific problems of the present study.

2.1.2 Radiation polymerization of vinyl monomers

Radiation induced polymerization of vinyl monomers is a direct application of radiation chemistry. Such syntheses of high polymers have been used for more than three

decades and now represent well established methods for producing a variety of polymers and copolymers. Radiation polymerization is not just a laboratory curiosity, but includes industrial applications. Its application to production of wood polymer composites (WPC), for example, is currently practiced commercially and under further development (30,55,56,90).

It is known that the initiation step in radical chain-growth polymerization reactions requires application of external energy. In radiation polymerization this energy is supplied by ionizing radiation from a source. Once the chain-growth reaction is started, however, the polymerization proceeds independent of the energy source according to conventional kinetic rules derived for chain-growth polymerization (22,36,42).

Main features of vinyl monomer radiation polymerization are basically similar to those of conventional heat-catalyzed free radical polymerization reactions. The chemical action of radiation is limited to the primary initiation step leading to production of free radicals and to a few peculiar secondary effects, such as degradation and crosslinking.

Radiation polymerization mechanisms have been described by Chapiro in an excellent monograph (22), as well as by others (24,42,74). In all these studies

features of radiation polymerization kinetics are discussed. In addition, the present study requires special emphasis on acceleration *via* gel-effect (Ge) phenomena in highly viscous and crosslinked structures.

2.1.2.1 Kinetic considerations

Kinetics of chain-growth polymerization is based on interpretation of experimental results from free radical reactions. At least three types of reactions are described (22) as:

i. initiation, which produces free radicals,
ii. propagation, which involves a sequence of identical reactions repeated many times, and
iii. termination, which stops the chain-growth reaction.

It is also possible that a single free radical may initiate formation of more than one polymer molecule through a reaction in which the active site, i.e., free radical, is transferred without loss of activity to another molecule in the system. This type of reaction is termed a chain-transfer reaction. Formation of macromolecules containing thousands of covalently bonded monomer units is an overall result of the above elementary reactions.

2.1.2.2 Overall rate of polymerization

The overall rate of vinyl monomer polymerization, i.e., the rate of monomer disappearance in the reaction system, was described (22,42) by the following kinetic scheme:

	Process:	Rates:
Initiation:	$X \longrightarrow 2\,R^{\bullet}$	R_i ...../2-1/
Propagation:	$R^{\bullet} + M \longrightarrow RM^{\bullet}$	
	$RM_x^{\bullet} + M \longrightarrow RM_{x+1}^{\bullet}$	$k_p/RM^{\bullet}/\cdot/M/$ ...../2-2/
Termination:	$RM_x^{\bullet} + RM_y^{\bullet} \rightarrow P_{x+y}$	$k_t/RM^{\bullet}/^2$ ...../2-3/

where: X = any molecule in the system,

$R^{\bullet}$ = primary radical,

M = monomer,

$RM^{\bullet}$ = growing polymer chain,

P = dead polymer,

R_i = rate of initiation,

k_p = rate constant for propagation, and

k_t = rate constant for termination.

After mathematical treatment and steady state assumptions, the overall polymerization rate (R_p) is given as:

$$R_p = k_p \cdot k_t^{-1/2} \cdot R_i^{1/2} \cdot /M/ \quad \ldots\ldots/2\text{-}4/$$

This classical equation indicates that rate of polymerization is proportional to the square root of initiation

rate. The quantity $k_p/k_t^{1/2}$, a constant value at steady state conditions, changes at higher conversion degree and accelerates the overall reaction rate. As a second consequence an increase in molecular weight (MW), or degree of polymerization (DP), is observed. This is required by the following equation (22):

$$DP = k_p/k_t^{1/2} \cdot R_i^{-1/2} \cdot /M/ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots /2\text{-}5/$$

With respect to a monomer of interest in this study, (MMA), the published results on polymerization kinetics fully confirm /2-4/ and /2-5/ (22,59,106). Bulk polymerization of MMA, especially to the high conversion degree, exhibits deviations from these theoretical predictions (6,22,64,75,87, 89,103).

2.1.2.3 Bulk polymerization of MMA

Much work has been done in the area of MMA radiation polymerization. The free radical mechanism for this reaction was established by Chapiro (22). He deduced the mechanism from data which showed that polymerization was inhibited by air and benzoquinone.

During initial reaction stages the polymerization process shows a characteristic Arrhenius temperature dependence, with an activation energy of 4.9 kcal/mole (3,22). The constant value of activation energy was observed over wide

temperature range (-18 °C to 70 °C) with dose rates 2.3 to 2.5 x 10^5 rad/hr . In a more recent work by Lipscomb and Weber (60), who operated between -49 and -19 °C and at a dose rate of 3.7 x 10^5 rad/hr, the activation energy was found to be 3.85 kcal/mole. It should be pointed out, however, that the freezing point of MMA is -48.2 °C (86), which casts doubt as to validity of the data at -49 °C.

The reaction controlled region is dose rate dependent. Chapiro (22) reported a dependence to the 0.5 power for low dose rates (less than 5.4 x 10^3 rad/hr). Above 10^6 rad/hr the reaction was said to be dose rate independent. Ballantine et al. (3) reported dose rate dependence of 0.5 up to 2.0 x 10^5 rad/hr. In contrast Lipscomb and Weber (60), working at approximately the same dose rate, reported a power factor of 0.33 at both -49 °C and -19 °C.

For MMA, as for other vinyl monomers, the mechanism of free radical polymerization changes drastically at high conversion degree. A special mechanism, which predominates and controls later stages of polymerization kinetics, has been attributed to Ge. Because of its particular importance to the present study, Ge phenomena are discussed in detail in a later section.

Attempts to define overall reaction orders have been unsuccessful due to effects associated with Ge phenomena.

Nevertheless, the MMA polymerization reaction is considered to be of zero-order up to about 20% conversion (12). Rabinowitch (83) derived an expression relating reduction of the termination rate constant with the rate of diffusion for second order reactions. Vaughan (104) and later Robertson (87) tried to correlate the experimental data for MMA and styrene using the Rabinowitch equation. The result, however, was unsatisfactory.

Attempts to quantify polymerization rates in the Ge region have been hampered by two major factors. Firstly, the onset of Ge does not occur at a specific conversion. Rather, conversion at which Ge begins is strongly dependent upon temperature. Secondly, experimental measurements in the Ge region are inherently difficult. Isothermal conditions are almost impossible to maintain,and analysis of the partly plasticized material requires special experimental techniques for recovery and solution of gels and isolation of the unconverted monomer.

2.2 Polymerization in Gel-Phase Media

The kinetic scheme of free radical polymerization, discussed in Section 2.1.2.2, applies only to the initial reaction stage up to approximately 5 to 10% conversion. If reactions proceed to higher conversion degrees the mobility of reactive species is reduced by a massive increase in local

viscosity. The rate of diffusion is significantly reduced. This phenomenon manifests itself in Ge, commonly observed in bulk polymerization of vinyl monomers, particularly with MMA (75,103).

The most important consequence of Ge is acceleration of the overall polymerization rate, as soon as some critical conversion level has been reached. If viscosity of the reaction medium is further increased, long range diffusion of polymeric radicals is suppressed and only local mobility of polymer segments ensures limited reaction. Finally, if the system sets to glass, all polymeric radicals remain immobilized and the residual reaction, if any, results only from diffusion of small unreacted monomer molecules.

Under a given set of reaction conditions various polymerization reactions may fall into any one of three cases as:

i. both propagation and termination are controlled by reaction rate,

ii. propagation is reaction-controlled and termination is diffusion-controlled, or

iii. both propagation and termination are diffusion-controlled.

The case of diffusion-controlled propagation and reaction-controlled termination is a physical impossibility,

since reaction between two polymer radical segments would be favored over reaction between monomer and polymer radicals.

2.2.1 Autoacceleration; experimental evidence for gel-effect (Ge)

Bulk polymerization of a number of vinyl monomers, such as MMA (6,13,62,75,87,89,103), methyl acrylate (MA) (15,64,65), butyl methacrylate (BMA) (14), S (8,39,87) and vinyl acetate (VA) (59), follow the patterns of autocatalytic reactions. The polymerization proceeds smoothly at first with constant rate, as expected from steady state kinetics /2-4/. After a critical conversion is attained the reaction rate suddenly increases several times. The reaction at this stage shows a definite autoacceleration character. For S polymerization, for example, the overall acceleration factor is 5.2 at 38% and 16.9 at 60% conversion (59). Similarly for MMA polymerization, the initial polymerization rate of 3.5%/hr increases to 15.4%/hr at 30% conversion and 24.5%/hr at 50% conversion (43) as shown in Table 2-1.

Simultaneously with increase in polymerization rate, several secondary effects are evident. These include increased MW and concomitant local temperature rise (22,36). These effects are explained by the decreased termination. It is generally accepted that reduction in the rate of termination is caused by reduced mobility of growing polymer chains in the viscous medium.

Measurements of individual rate constants, Table 2-1 (43), show that the decrease in termination rate occurs at fairly low conversion, generally between 10 to 30%. On the other hand, the propagation rate is enhanced only after 50 to 60% conversion, i.e., after the reaction mixture has already gelled. This is in accordance with theoretical conclusions drawn by Rabinowitch (83). He concluded that reactions having low activation energies are more likely to become diffusion-controlled. An average activation energy for termination is 0 to 2 kcal/mole, while activation energy for propagation is 5 to 8 kcal/mole (22,23,36). A similar conclusion was reached by Vaughan (104) who calculated critical viscosities for elementary reaction steps. His critical viscosities for termination and propagation were 2.0 and 7.0 x 10^5 poise, respectively. It must be emphasized, however, that the viscosity effect is not due to changes in radical reactivities. Instead, it arises from a purely physical effect caused by the diffusion barrier.

Hayden and Melville (43) studied variation of several MMA polymerization parameters with conversion, including average lifetime of a kinetic chain and rate constants for both propagation and termination. They pointed out that the termination rate constant decreased by about 100,000-fold from the start of polymerization up to 50% conversion. The effect of conversion on kinetic variables has been divided into three distinct stages as:

i. Stage I, up to 10% conversion,

ii. Stage II, between 10 to 70% conversion, and

iii. Stage III, over 70% conversion.

In Stage I the reaction mixture changes from a mobile liquid to a viscous syrup, but the rate of polymerization adheres to steady state kinetics represented by /2-4/.

In Stage II the reaction mixture changes from a very viscous fluid to a soft solid. Large increases are obtained in both polymerization rate and lifetime of the kinetic chains. Both increase by approximately ten fold.

In Stage III as conversion nears completion, termination appears to become a unimolecular process and even propagation becomes diffusion-controlled as molecules are immobilized in the gel-glassy reaction medium.

Although propagation in gel is hindered, the overall effect is much smaller since k_p values are smaller than k_t by a factor of 10^4 to 10^5 (Table 2-1). Termination involves the reaction of two large polymer segments /2-3/, while in propagation only one large polymer radical and a small monomer molecule are involved /2-2/. High viscosity affects the former much more than the latter. Therefore, the quantity $k_p/k_t^{1/2}$ changes during the polymerization process. This results, in accordance with /2-4/, in an increase of the overall polymerization rate with increasing conversion. As a

second consequence, and in accordance with /2-5/, an increase in molecular weight is obtained. This has been verified experimentally also for numerous vinyl monomers (13,14,78).

Solvents and chain-transfer agents, which directly reduce viscosity and molecular weight of polymer products, delay or even eliminate the onset of Ge. As shown by Schultz and Haborth (89), autoacceleration is completely eliminated when the reaction system is diluted with 60% of an inert solvent. Molecular weight of polymer formed in different solutions also decreases with increasing dilution. This is the result of decreased kinetic chain lifetime due to bimolecular chain termination (6,103). It was further shown that addition of an inert polymer, which increases viscosity of the reaction media, brought about a premature appearance of Ge (103).

Temperature changes of reaction media were measured by several investigators. It was noted that acceleration is accompanied by considerable overheating of the system. In order to avoid additional complications, such as created by non-isothermal conditions, Schultz and Harborth (89) polymerized thin layers of MMA onto a mercury surface. Results of this experiment conclusively demonstrated that Ge acceleration is a truly kinetic phenomenon.

Temperature rise at the onset of Ge is much more pronounced with MMA than with S (3), even at very low polymerization temperatures, e.g., -18 ^{o}C. Difunctional methacrylates

and acrylates, irradiated in solid state, showed remarkable temperature rise even at -90 °C reaction temperature (22).

A direct consequence of Ge in polymerization under constant rate of initiation is that the concentration of growing polymer chains increases with time. Thus the polymerization system does not follow stationary kinetics due to violation of the steady state assumption. Overall polymerization rate is not proportional to the square root of initiation /2-4/. Indeed, a marked departure from conventional kinetics is observed and the reaction order with respect to initiation rate rises above the theoretical 0.5 value. A complete treatment of Ge kinetics should take into account both the gradual decrease of termination rate and the concomitant increase in free radical concentration. Such a treatment is still lacking (23).

Reduction in the termination step in free radical polymerization, and consequently premature onset of Ge, can be brought about by several physical methods. All these methods are based on the principle that termination by the mutual reaction of two polymer chains can be prevented by isolating the growing polymer segments from each other. In many cases, isolation of growing polymer fragments has been accomplished by "occlusion" of the active end groups within discrete polymer particles. This phenomenon is responsible for the unusual rate behaviour observed in the following systems (59):

i. polymerization reactions initiated in gas phase,

ii. polymerization of a monomer in a medium which is non-solvent for the resulting polymer, termed precipitation polymerization,

iii. emulsion polymerization,

iv. polymerization of crystalline monomers in the solid systems, and

v. polymerization within crosslinked networks, such as vinyl-divinyl comonomer systems.

Systems ii, iii and v are far the most important, particularly for practical applications involving WPC, as well as paper polymer composites (PPC).

If polymerization is carried out in a medium in which the resulting polymer is insoluble, the growing polymer chains separate from the solution to form a second phase by precipitation. Reaction proceeds thereafter in heterogeneous medium and usually shows a peculiar behaviour similar in many respects to Ge. Systems which behave in this manner include:

i. pure monomers which do not dissolve their own polymer, for example acrylonitrile (AN) and vinyl chloride (VC),

ii. monomer solutions immiscible with solvents which are precipitants for the polymer, e.g., methanol-S, methanol-MMA, hexane-VA, and

iii. comonomer mixtures which do not dissolve the resulting copolymer, as the AN-S comonomer system.

Acceleration during early reaction stages, a phenomenon identical with Ge, has been interpreted as impeded termination in the presence of a polymer precipitant (1,16, 22,75). Here relative conversion rate is a function of monomer/precipitant ratio. Maximum acceleration is observed at precipitant content slightly below the precipitation point where phase separation leads to a viscous, gel-like coagulate, highly swollen by monomer. The overall polymerization rate, at this point, rises sharply and the reaction exhibits non-steady state kinetics.

Physical state of the precipitated polymer and the extent of swelling seem to be very important factors in preparation of graft copolymers (21). Thus, it has been reported that a highly swollen substrate is necessary to form large amounts of graft copolymers, e.g., increased grafting efficiency (21,49,57,96).

The alcohol-S system has been used in applied studies for radiation cured WPC. Siau et al. (90) compared grafting efficiency of S on red pine (Pinus resinosa Ait.), as well as on yellow-poplar (Liriodendron tulipifera L.). Ramalingam et al. (85) evaluated effects of a three component system,

methanol-S-water, on graft copolymerization efficiency. They concluded that,in addition to the observed acceleration effects, this system increased grafting efficiency. This is in accordance with theoretical conclusions drawn from radical lifetimes observed in viscous and swollen systems (21,43).

2.2.2 Acceleration within the crosslinked network; copolymerization of vinyl-divinyl comonomer systems

In many copolymerization reactions divinyl compounds are used as monomeric constituents. The obvious reason for including such compounds is to obtain crosslinks between linear macromolecules. This leads to three-dimensional networks.

When divinyl monomers (DVM) are incorporated in a comonomer system, only one of the double bonds reacts(1). The other is left as a pendant vinyl group. At higher conversion degree the pendant vinyl group may be involved in propagation reactions. At such stage a rather abrupt transition is experienced in passing from the liquid to gel state. If sufficient polyfunctional crosslinking agent is used, a significant departure from linearity in the overall polymerization rate can be achieved during early reaction stages due to a premature onset of Ge phenomena. Increase in polymerization rate is a direct consequence of reducing the termination reaction step by isolating the growing polymer radical segments in crosslinked three-dimensional networks (59).

The formation of such a network,resulting in gelation of the comonomer mixture, generally takes place over a very narrow conversion range and varies inversely with both the amount of crosslinking agent and average DP (34,36,97,105). Flory (34) outlined a general method for determining and predicting the extent of reactions in which such a network is possible and carried out a detailed calculation,for the case of polycondensation reactions. His calculations were in good agreement with experimental results. He indicated that a similar method may be applied to addition polymerization, particularly for vinyl-divinyl comonomer systems in which all vinyl groups have the same reactivity.

2.2.2.1 Crosslinking and gelation; prediction of gel-effect (Ge)

According to Flory's treatment on polycondensation reactions, Ge in monovinyl and divinyl comonomer mixtures in which all vinyl groups have the same reactivity may be calculated from the functionality equation (34):

$$p = 2/f - 2/f \times DP \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad /2\text{-}6/$$

where:

p = extent of reaction,

f = average functionality,

DP = degree of polymerization,

For a very large DP, which is always the case in addition polymerization, /2-6/ reduces to:

$$p = 2/f \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad /2\text{-}7/$$

With bifunctional monomer molecules, as a consequence of /2-7/, gelation does not occur. With tri- and tetra-functional molecules gelation occurs at 66 and 50% conversion, respectively. However, practical experimental results do not correlate with predicted values. Large deviations from theoretical values were observed even for polymerization of related monomers such as VA-vinyl succinate (VS), MMA-EGDMA, or S-divinyl benzene (DVB) (97,105). Explanation of these deviations, as pointed out by Flory (36) and Walling (105), lies mostly in two factors:

i. application of the condensation polymerization functionality equation to chain-growth polymerization systems, and

ii. excessive occurrence of intra-molecular crosslinking before onset of Ge, where wastage of inter-molecular crosslinks in this manner is neglected by theory.

Alfrey et al. (1) concluded that crosslinking and subsequent gelation depends on relative reactivities of two double bonds in DVM. The point at which Ge occurs has been treated mathematically for several comonomer systems. In all

instances it has been assumed that DVM was present in a low concentration, since this is the case encountered in most practical applications.

Generally, three cases were considered (1) according to type of crosslinking agent, as well as vinyl monomer used:

i. Case I, copolymerization of symmetrical DVM with a vinyl monomer of equal reactivity,

ii. Case II, copolymerization of a symmetrical DVM with a vinyl monomer of different reactivity, and

iii. Case III, copolymerization of an unsymmetrical DVM with vinyl monomer of different reactivity.

In Case I all double bonds have the same reactivity and chemical structure. Examples of such a system are:

i. MMA-EGDMA,

ii. VA-vinyl adipate (VAD), and

iii. S-DVB.

In Case II the reactivity and structure of double bonds in DVM differ from the double bond character in the vinyl monomer. An example of this system is S-EGDMA or MMA-DVB. Acceleration in this system was studied previously (70).

In Case III the two double bonds in dienes have different structures and reactivities. An example of this type is MMA-allyl methacrylate (AMA). This system is very complicated and inefficient. Allyl type double bonds have generally lower reactivity, thereby crosslinking and Ge occur only after considerable conversion has been attained.

In some cases reaction of one double bond in the diene results in a marked reduction in reactivity of the remaining double bond. The overall effect is a marked delay in Ge. An example of this is copolymerization of vinyl monomers with 1,3-dienes. The 1,4 polymerization of diene leads to residual 2,3 double bonds, which have lowered reactivity (1). The most studied dienes of this type are isoprene, butadiene and chloroprene (1,44,58,95).

Much experimental material has been accumulated on copolymerization of symmetrical DVM with vinyl monomer of identical double bond structure (Case I). Results derived from experimental data on gelation were in good agreement with predicted values (1) only within a limited DVM concentration range. There has been some controversy about these discrepancies (97,105).

Storey (97) studied the acceleration efficiency of DVB in the S-DVB comonomer system using heat-catalyst. He found that initial polymerization rate varied linearly with

DVB concentration at both temperatures studied (70 °C and 87 °C). The MMA-EGDMA system was studied by Walling (105). He also examined the VA-VAD system. In all studies at higher DVM concentration agreement between expected results and those obtained was poor. The discrepancy may have arisen in part from intra-molecular chain cyclization reactions (17,18,19,38, 40,41,61,92) which prevent DVM participation in inter-molecular crosslinking. Walling (105), however, did not consider this to be a major factor. He interpreted his results in terms associated with diffusion-controlled crosslinking reaction. According to his hypothesis, rate coefficient of the cross-linking process decreases with increasing DVM concentration.

Simpson et al. (91) showed that a considerable fraction of DVM is used in the intra-molecular cyclization reaction. This resulted in delayed gelation at comparatively high conversion degrees. Subsequently, Gordon and Roe (40) examined application of the classical gelation theory to the MMA-EGDMA comonomer system. They concluded that this theory was applicable to their results only if further allowances were made for internal cyclization. Further, diffusion controlled crosslinking, as described by Walling (105), was unimportant until after Ge had been passed.

Later, Holt and Simpson (48) estimated the extent of inter-molecular cyclization on a series of diallyl esters. All monomers studied gave rise to chain cyclization under

similar reaction conditions. The tendency of monomers to cyclize was found to be controlled by the molecular distance between double bonds in the difunctional monomer. This has not been considered as a significant factor in gelation kinetics.

2.2.2.2 Influence of divinyl monomer molecular bridge length

It may be theorized that polymerization kinetics of vinyl-divinyl comonomer systems and properties of the polymer products from such systems are determined not only by the nature of reactive groups, but also by the chemical structure and dimension of the DVM molecular bridge, i.e., the molecular fragment connecting double bonds in the DVM. Divinyl monomers having considerable molecular bridge length have higher viscosities. This may have an indirect effect on diffusion processes and polymerization kinetics, particularly in connection with gelation and acceleration via Ge.

From experimental data collected for other purposes in (48,61) and from other studies (7,8,9,57,58,76,77) an inference can be made as to the importance of molecular distance between DVM double bonds. This is based on:

i. competition between inter-molecular and intra-molecular propagation as related to the ring size, i.e., cyclization versus cross-linking; and

ii. overall polymerization kinetics, e.g., numerical values of individual rate constants, as well as overall polymerization rate.

The importance of intra-molecular cyclization was emphasized when Butler and co-worker (18,19) found that radical polymerization of diallyl monomers gave soluble, non-crosslinked polymers with little or no residual unsaturation. Extensive work by Simpson and co-workers (48,91,92) has helped to show that the size of ring structure which can be formed, determines whether inter-molecular polymerization or intra-molecular cyclization is the predominant reaction for a particular monomer. As a rule, the formation of 6-membered rings is appreciably greater than those of larger size (59,78). Contrary to expectations, however, ring structures containing as many as 11 and 17 atoms have been reported (17,38,48,61).

The influence of molecular bridge length on polymerization kinetics and numerical values of individual rate constants has not been studied systematically. Only limited data are available. Recently, however, Soviet scientists (7,8,9,57,58,76) have published comprehensive studies on polymerization kinetics and properties of such polymers.

Berlin (8) calculated individual rate constants of dimethacrylate esters of alkyleneglycols having the general formula:

$$CH_2 = \overset{CH_3}{\overset{|}{C}} - COO -(CH_2)_x - OOC - \overset{CH_3}{\overset{|}{C}} = CH_2$$

where: x = 4, 6, 10.

The initial polymerization rate and propagation rate constants sharply increased with length between double bonds. The absolute k_p value for MMA was 300 l/mole. sec and increased to 600, 1,200, and 1,880 l/mole. sec for monomers with x equal to 4,6, and 10 respectively (Table 2-2). At lower and average conversions, k_p for these compounds exceeded k_p for MMA by 5-10 times, although true MMA radical reactivity and the double bonds of methacrylate esters do not depend on the nature of glycol or ester residues (12).

From Table 2-2 it is evident that the initial polymerization rate for all oligomers exceeds polymerization rate for MMA even at 50% conversion where viscosity of the polymerization mixture is much higher. The reason for higher polymerization rate is obvious from the numerical value of $k_p/k_t^{1/2}$. Simple calculation of $k_p/k_t^{1/2}$, from data at zero conversion for esters with x equal to 4, 6, and 10 gives 67, 152 and 290 x 10^{-2}, respectively. All these values are significantly higher than the maximum value found for MMA as demonstrated in Table 2-1 (43). Similar increase in initial polymerization rate was pointed out for polymerization of dimethacrylates and mixed allyl and carboxyallyl esters, such as (8):

$$R_1 - O - (CH_2-CH_2-O)_{1-3} - R_2$$

where: R_1 is: $CH_2 = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - CO-$

R_2 is: $CH_2 = CH - CH_2 - COO$, or

$CH_2 = CH - CH_2 - O -$

The increased reactivity with increase in molecular bridge length between double bonds was attributed to multiple ether bonds which increased flexibility of the three-dimensional framework. Because flexibility of these molecules favours tight packing, double bonds of acrylate groups are drawn together and are arranged in a "kinetically-favourable" pattern and form "bundle associated swarms" similar to nematic formation in liquid crystals (8). The transformation from liquid polymerizable esters to space-regular crystalline arrangements indicates broad possibilities of directed synthesis and regulation of both polymerization kinetics and properties of the resultant polymer products.

2.2.2.3 Accelerated polymerization in forming wood polymer composites (WPC)

Much work has been published in connection with application of vinyl monomers to wood and papers. Both radiation and heat catalyst techniques of polymerization have been used (4,5,30,31,33,49,53 - 56,82,84,85,90,93,96,101). This simple process converts wood into WPC, a composite material with improved physical properties such as hardness, abrasion resistance and compression strength. Further, dimensional stability and associated wet strength properties are improved. So far MMA and S have been the most widely used monomers for this purpose.

Problems with *in situ* radiation polymerization of vinyl monomers relate to radiation sensitivity of wood constituents, particularly cellulose. Vinyl monomers, such as S require massive dosages (10 Mrad) for complete polymerization. The large dose requirements are necessary mainly because of low G-value, 0.6 (22). It is also expected that monomers associated with wood components require more energy for polymerization due to influence of wood components and oxygen in the wood structure.

It is known (22) that chlorinated compounds, such as CCl_4, accelerate radiation polymerization of vinyl monomers. The method has been used for reducing dose requirements in production of WPC (30,55,82,93). However, secondary effects caused by CCl_4, particularly since it functions as a very efficient chain-transfer agent (22,42,59), are disadvantageous and limit practical value of CCl_4 acceleration technique (30,82).

Addition of crosslinking monomers, which contain two or more vinyl groups, to common vinyl monomers allows copolymerization and formation of three-dimensional networks. In addition to improved WPC physical properties (30,66), crosslinking agents quickly turn liquid monomers, deposited in the wood void spaces, into gels and thus:

i. accelerate the polymerization via Ge, and
ii. eliminate large monomer losses due to evaporation.

So far, only scant attention has been given to the accelerating ability of different divinyl monomers. A systematic study on gelation kinetics in vinyl-divinyl comonomer systems is lacking.

Raff et al. (84) investigated the effect of 5% DVB on radiation polymerization of S in WPC. They found that presence of the crosslinking agent increased the conversion degree for a particular dosage. Unfortunately, other comparative data were not given.

Kent et al. (55) proposed addition of a DVM (EGDMA) for the purpose of increasing molecular weight, as well as acceleration of radiation polymerization. EGDMA was examined as additive to MMA. However, the minor accelerating effect at 2% concentration was not very convincing.

Kenaga (53) discussed heat-catalyst polymerization with a series of vinyl-divinyl and vinyl-trivinyl comonomer systems. Effect of crosslinking agents on polymerization of t-butyl styrene (TBS) in basswood (Tilia americana L.) at 90°C was followed by the time-temperature exotherm method for DVM concentrations up to 30%. Based on evidence provided by his study trimethylol propane triacrylate (TMPTA) was selected as the most effective accelerator. Several dimethacrylates were shown to be more effective than DVB. The latter contain small amounts of diethyl benzene which remained trapped in wood and caused odor problems.

In 1969 Paszner (79) introduced and found TEGDMA to be a very effective crosslinking agent and accelerator for radiation polymerization of MMA and S. Dose requirements for complete polymerization, as followed by the time-temperature exotherm method, were found to be lower than that for an optimum mixture of S-AN. Subsequently, the accelerating ability of TEGDMA was tested systematically in numerous other comonomer systems (11,25,26,52,67-71,79-81,98,99).

Recently, Duran and Meyer (33) adopted a systematic approach for evaluating the accelerating ability of trimethylol propane trimethacrylate (TMPTMA) with MMA in basswood composites. Using maxima of time-temperature exotherm curves (31) as indicators of reaction rates showed that time to exotherm peak decreased rapidly as percentage of crosslinking agent increased across low concentration levels (1-20%). They attributed the increase in reaction rate, i.e., the decrease in time to exotherm peak, to formation of a three-dimensional gel structure.

In our laboratories, as reported earlier (68-70,79-81, 98) time-temperature exotherm curves were used for quantitative characterization of accelerating ability of crosslinking agents in radiation polymerization of vinyl-divinyl comonomer systems. The most attractive comonomer systems have been applied to fabrication of WPC, PPC and veneer polymer composites (VPC), as well as proposed for tough, highly resistant surface coatings (25,26,52,79-81,98,99).

In summary, much work has been done to clarify Ge acceleration phenomena in vinyl monomer homopolymerization. Vinyl-divinyl comonomer systems, however, have not been studied systematically. It is clear that theoretical treatment of Ge during polymerization of vinyl-divinyl comonomer systems is more complex than that accepted for condensation polymerization. Acceleration *via* crosslinking agents is based not only on statistical treatment of crosslink probabilities, but involves many other factors, such as intra-molecular cyclization, diffusion, reaction conditions and chemical structure of divinyl monomers. As example, the molecular bridge length between double bonds may have significant effects. Much work remains to be done before Ge is understood in vinyl-divinyl systems.

3.0 MATERIALS AND METHODS

Methods and some monomers used in this study were described in detail earlier (67,69,79). Only general monomer characteristics, brief definitions of polymerization parameters, as well as thermomechanical and physical-mechanical tests for polymer products are repeated below.

3.1 Monomers

Two kinds of monomers were used in this study. The vinyl monomer was methyl methacrylate (MMA), while a commercially available series of glycol dimethacrylates were used as divinyl monomers.

3.1.1 Methyl methacrylate

Methyl methacrylate was the basic monomer used in all experiments. It contained a commercial inhibitor (50 p.p.m. hydroquinone) as supplied by Eastman Co. No monomer purification was attempted for these experiments.

3.1.2 Divinyl monomers

Four different divinyl monomers (DVM) of the common glycol dimethacrylate structure, with various molecular chain

lengths between terminal vinyl double bonds, were selected. These comonomers served as crosslinking agents and accelerators for MMA polymerization. All DVM are characterized by the general formula:

$$CH_2 = \overset{CH_3}{\overset{|}{C}} - CO -(O - CH_2 - CH_2 -)_n - O - OC - \overset{CH_3}{\overset{|}{C}} = CH_2$$

The index "n" varied from 1 to 4. The four DVM used in this study were:

i. Ethylene glycol dimethacrylate (EGDMA),
ii. Diethylene glycol dimethacrylate (DEGDMA),
iii. Triethylene glycol dimethacrylate (TrEGDMA), and
iv. Tetraethylene glycol dimethacrylate (TEGDMA).

Properties of the MMA and DVM used are given in Table 3-1. All DVM were purchased from Borden Chemical Co., Philadelphia, Pa. Higher homologs of the series were not available at the time.

3.1.3 Calculation of structural parameters

To transfer from monomer into polymer, each carbon atom in the polymer chain or in the three-dimensional network must be connected to at least two other atoms by covalent bonds. Linear one-dimensional (thermoplastic) macromolecules, such as poly(MMA) for example, only contain 2-way connected carbon atoms and thus have a connection number (CN) equal to

2.000. Thermosetting, crosslinked polymers or copolymers contain both 2-way and 3-way connected carbon atoms. Their CN is between 2.000 and 3.000.

Recently, Holliday and coworker (45,46) proposed and demonstrated the usefulness of CN for simple topological analysis of random polymer networks. CN describes an average structural feature of polymers and can be extended further to predict physical properties of polymer products.

An average CN can be calculated from the chemical structure of monomer repeating units as:

$$CN = \frac{2a + 3b + 4c}{a + b + c} \qquad \text{.....(3-1)}$$

where: a, b and c are, respectively, 2-way, 3-way and 4-way connected atoms in the repeating monomer units. Calculated values for members of the present series are given in Table 3-1.

The average CN can be extended further to copolymers as copolymer connection number (CN_{co}). CN_{co} provides an average number of network bonds, i.e., crosslinking density. The numerical value of CN_{co} depends on molar composition of the comonomer mixture. It is calculated as:

$$CN_{co} = (CN_{MMA} \times mf_{MMA}) + (CN_{DVN} \times mf_{DVM}) \qquad \text{.....(3-2)}$$

where: CN_{MMA} and CN_{DVM} are connection numbers for MMA and DVM,

mf_{MMA} and mf_{DVM} are mole fractions of MMA and DVM in the comonomer system, respectively.

In calculating an average CN_{co} only those connections are considered which form part of polymer network. Thus, side substituents such as CH_3- or CH_3OOC- in poly(MMA), for example, were excluded.

3.1.4 Preparation of comonomer mixtures

Mixtures of MMA and respective DVM were prepared on a volume/volume basis in lots of 50 ml to minimize experimental error due to mixing. These were stored at -10 °C prior to polymerization. Volume concentrations, as well as mole ratios are given in Table 3-2.

Relative viscosities (η_{rel}) of the pure monomer and comonomer mixtures were measured with a Ubbelohde $I/_a$ viscosimeter (K = 0.05394) at 25 °C and calculated as:

$$\eta_{rel} = \frac{t_{mixture}}{t_{MMA}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots /3\text{-}3/$$

where: $t_{mixture}$ and t_{MMA} are efflux times for the comonomer mixture and MMA, respectively. Relative viscosities for pure monomers are given in Table 3-1 and for the comonomer mixtures in Table 3-2.

3.2 Radiation Polymerization Technique

Although radiation induced polymerization is now a well established technique, only scant attention has been given to polymerization kinetics as related to Ge and production of WPC. One reason has been lack of proper methods for following the transformation of monomers to polymers, especially within the radiation field. Difficulties in studying polymerization kinetics to high degree of conversion are well documented.

Davies et al. (31) studied the kinetics of MMA radiation polymerization in yellow birch (Betula alleghaniensis Britt.) and red pine (Pinus resinosa Ait.) by a method previously described for heat-catalyst bulk polymerization of vinyl monomers (5,88). In his study the exothermic heat released during polymerization was recorded automatically. From the shape of time-temperature exotherms, kinetically important stages of polymerization were derived and these were related to inhibition, Ge phenomena and complete conversion at peak temperature. The same technique was adopted for this study. Detailed descriptions and determination of polymerization parameters have been given previously (67,69,70).

3.2.1 Definition and determination of polymerization parameters

The temperature (T), ^{o}C versus time (t), min records obtained, such as shown in Fig. 3-1, were analysed to provide the following polymerization characteristics:

i. Initial condition of the system (T_{36}, t_o);

ii. "Gel-Effect Point" (GEP) by geometric solution (Fig. 3-1) as the exotherm curve intersection by the perpendicular through the common point obtained by extrapolating early and late curve stages, and with components (T_{GEP}, t_{GEP});

iii. "Cure" at the exotherm maximum (MAX) with components (T_{MAX}, t_{MAX});

iv. "Activation" (I) period as time interval to reach GEP and calculated as ($t_{GEP} - t_o$), and

v. "Acceleration" (II) period as time interval between GEP and the exotherm maximum, and calculated ($t_{MAX} - t_{GEP}$).

As shown also in Fig. 3-1, dose (D) may be substituted for time (t), thereby describing the irradiation requirements at the single dose rate examined in the present study.

To compare relative rates of polymerization in "Activation" (I) and "Acceleration" (II) periods, the following polymerization coefficients (PRC) were calculated:

i. Polymerization rate coefficient for the "Activation" (PRC_I) period as:

$$PRC_I = \frac{T_{GEP} - T_{36}}{t_{GEP} - t_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots /3\text{-}4/$$

ii. Polymerization rate coefficient for the "Acceleration" (PRC_{II}) period as:

$$PRC_{II} = \frac{T_{MAX} - T_{GEP}}{t_{MAX} - t_{GEP}} \quad \ldots\ldots\ldots\ldots\ldots\ldots /3\text{-}5/$$

The ratio of these coefficients, PRC_{II}/PRC_{I}, numerically expresses the increase in polymerization rate due to the Ge phenomena.

Reciprocal of time needed to attain exotherm maximum ($1/t_{MAX}$) is used as a measure for characterizing the overall curing rate (OCR):

$$OCR = \frac{1}{t_{MAX}} \quad \ldots\ldots\ldots\ldots\ldots\ldots /3\text{-}6/$$

By analogy, reciprocal of the time to reach GEP ($1/t_{GEP}$), refers to the overall gelation rate (OGR) and characterizes the efficiency of the crosslinking agent to onset Ge phenomena.

3.2.2 Polymerization procedure

For determination of polymerization parameters 5 ml of monomer or comonomer mixture (volume/volume) were placed in a small glass vial, which was then flushed with nitrogen and

sealed. Radiation polymerization was done in a Gammacell 220 with dose rate at 0.82 Mrad/hr, as determined by Fricke dosimetry (27). In two experiments, radiation dose rate attenuators were used to evaluate influence of dose rate on OCR.

Comonomer mixtures were first conditioned to the ambient Gammacell chamber temperature (36 °C), then set in a styrofoam seat which provided thermal insulation and reproducible position in the chamber. In each case, exotherm temperatures were followed by insert copper-constantan thermocouples, with signals sent to a time based stripchart recorder calibrated against an ice-water reference junction. A similar technique has been described in detail (67,71). Use of the method involves assumptions that polymerization rate relates to heat evolution and that comparisons may be made between the systems studied.

3.2.3 Reproducibility of experimental results

Reproducibility of polymerization parameters, as derived from radiation polymerization exotherms by three independent operators, with the MMA-TEGDMA comonomer system (11), was tested on sixteen identical experiments, done as described above. The following standard deviation values were calculated (50):

i. $t_{GEP} = 17.5 \pm 1.5$ min,

ii. $t_{MAX} = 23.2 \pm 1.7$ min,

iii. $T_{GEP} = 68.0 \pm 2.5$ °C, and

iv. $T_{MAX} = 148.0 \pm 7.8$ °C.

3.3 Properties of Polymer Products

Properties of polymer products were evaluated on the basis of their thermomechanical and mechanical strength behaviours. The individual characteristics, determined from unconventional thermomechanical curves, as well as standard compression stress-strain curves are described below.

3.3.1 Thermomechanical properties

Thermomechanical properties of the polymer products were obtained by a simple device constructed for recording deformation of loaded and heated specimens (67,69,80). Polymer samples (3 mm high) were rested on a tube support and were loaded *via* a rod 3.2×10^{-2} cm^2 in cross-section. The rod extension was coupled with a probe leading into the core of a linear variable differential transducer. High-temperature silicone oil was used as heating medium. The oil temperature was regulated to increase the sample temperature at constant rate (12 to 15 °C/min), followed by an insert copper-constantan thermocouple. Signals generated by changes in temperature and position of the transducer probe were fed to a recorder in the X-Y mode.

Glass transition temperature (T_g) and thermal distortion temperature (TDT) were determined as demonstrated in Fig. 3-2. In addition, the magnitude of relatively constant deformation across the broad rubbery state temperature range, characteristic of crosslinked polymers, was used to calculate thermomechanical deformation degree (TDD). As calculated here, TDD varies from 0 to 1 for thermoplastic to fully crosslinked polymer products. Numerical values of TDD were calculated as:

$$TDD = \frac{h - dp}{h} \quad \text{.....} \quad /3\text{-}7/$$

where: h = sample height, mm, and
dp = depth of probe penetration, mm.

The linear thermomechanical deformation coefficient (LTDC) was calculated according to Holsworth (47) as:

$$LTDC = \frac{k \times s}{h} \quad \text{.....} \quad /3\text{-}8/$$

where: k = the sensitivity (mils/inch of recorder chart paper),
s = slope of thermal deformation curve in the transition region (Fig. 3-2), and
h = sample height.

3.3.2 Mechanical strength properties

Stress-strain characteristics in compression were determined on a 5,000 kg capacity INSTRON Model TM-L Universal Testing Instrument. It was equipped with a CCM load cell and standard potentiometric-type graph recorder (51). The following testing conditions were used for all samples:

i. cross-head speed at 0.1 cm/min,
ii. recorder chart speed at 1.0 cm/min, and
iii. full scale load at 5,000 kg.

Standard compression test specimens were manufactured as cylinders from cured polymers. Polymerizations were done in a separate experiment with 10 ml of monomer or comonomer mixture. The sample length to diameter ratio was 2:1, according to ASTM Standard D 695-68T for determination of compressive properties of rigid plastics (2).

Test specimen dimensions with uniform circular cross-sectional area, as machined on a metal lathe, were as follows:

i. diameter = 1.0 cm,
ii. height = 2.0 cm,
iii. radius of gyration = 0.25, and
iv. slenderness ratio = 8.0

Various types of stress-strain curves, obtained with different polymers, and standard nomenclature are shown in Fig. 3-3 (20,72).

4.0 RESULTS

Radiation polymerization of the MMA-TEGDMA comonomer system was investigated over the concentration range 100:0 to 0:100. Results for individual polymerization parameters of these mixtures, as derived from polymerization exotherm curves, are summarized in Tables 4-1 and 4-2. Graphical interpretations for some of these results are given in Fig. 4-1 and 4-2. The relation between OCR ($1/t_{MAX}$) and TEGDMA volume concentration in MMA-TEGDMA comonomer mixtures is plotted in Fig. 4-3.

Results with the MMA-TEGDMA comonomer system demonstrated that most acceleration was obtained within a narrow concentration range, especially between 2.5 to 10% DVM concentration. At higher TEGDMA concentrations OCR was not proportional to volume concentration of the crosslinking agent. For this reason emphasis in further experiments was placed only on studying DVM concentrations up to 30% in comonomer mixtures. Accordingly, polymerization characteristics for MMA with the other three crosslinking agents are summarized in Tables 4-3 and 4-4. Graphical interpretation of t_{MAX} and t_{GEP}, as functions of DVM concentration in these systems, is given Fig. 4-4 and 4-5. Polymerization rate coefficients in "Activation" (PRC_I) and "Acceleration" (PRC_{II}) periods as a function of DVM concentration are plotted in Fig. 4-6.

Illustrations in Fig. 4-7 show the relationship between t_{MAX} and time required to onset Ge (t_{GEP}) for the four systems studied, including results with the S-TEGDMA system as taken from earlier work (70).

The OCR ($1/t_{MAX}$) increased proportionally with DVM concentration. Linear relationships between OCR and DVM concentration for the four systems are given in Fig. 4-8. For comparison, OCR values as calculated from results of Duran and Meyer (33) are included.

The ($1/t_{MAX}$ /DVM_{conc}) proportionality constants calculated from slopes in Fig. 4-8 represent the overall acceleration constant (K) for individual DVM. These are inversely related to DVM connection number (CN_{DVM}) as seen in Fig. 4-9.

The linear relationship between OCR and DVM concentration allows calculation and prediction of curing times (t_{MAX}) for MMA-DVM mixtures. Differences between measured and predicted curing times for the four systems at low DVM concentrations are summarized in Table 4-5. Similar calculations for the S-TEGDMA comonomer system are given in Table 4-6 as taken from earlier work (70).

The rather good agreement between predicted and experimentally measured curing times for different comonomer systems of the present and previous (70) studies suggested

further application of this new technique to published heat-catalyst results. Such data from quite dissimilar experiments (53) are examined in Table 4-7. Further, OCR as a function of crosslinking agent concentration for these data is demonstrated in Fig. 4-10.

Differences between heat-catalyst curing times published by Duran and Meyer (33) and calculated by the new method are given in Table 4-8. The overall acceleration constant and predicted curing times were calculated only from two randomly chosen experiments (the "two-point method").

One problem encountered with the heat-catalyst curing process is that reaction temperatures are virtually uncontrollable and peak temperature increases very rapidly up to 180-190 ^{o}C (53). Table 4-9 demonstrates that, using a controlled radiation curing method, polymerization rate can be altered over wide range and the associated peak exotherm temperature can be considerably reduced. The OCR varied linearly with the square root of radiation dose rate, as demonstrated in Fig. 4-11.

Shapes of thermomechanical curves, obtained by a simple device used are reproduced for MMA-EGDMA and MMA-TEGDMA systems in Fig. 4-12 and 4-13, respectively. Thermomechanical parameters such as T_g, TDD and TDT, as well as crosslinking density as represented by copolymer connection numbers (CN_{co}),

are given in Table 4-10 for the four systems studied. T_g, TDT and TDD relate mobility of heated polymer segments. Variation of these parameters with crosslinking density, calculated as CN_{co}, is represented in Fig. 4-14 and 4-15.

LTDC characterizes deformation rate in the transition region. The exponential relationship between LTDC and DVM concentration for the two extreme systems is illustrated in Fig. 4-16. The relationship between LTDC and CN_{co} for the four systems is given in Fig. 4-17.

Compression stress-strain curves for products from the MMA-EGDMA comonomer system are simulated in Fig. 4-18. For comparison similar curves for the MMA-TEGDMA system are shown in Fig. 4-19.

Numerical values for some physical-mechanical parameters of the polymer products, as derived from compression stress-strain tests for the four systems examined, are summarized in Table 4-11. Relationships between compression stress at rupture, compression strain at rupture and area under the stress-strain curve as an estimate of toughness, and DVM concentraion, are shown for the various systems in Fig. 4-20 to 4-23. Compression stress at rupture, as a function of CN_{co} for the four systems examined, is given in Fig. 4-24.

The slope of the initial straight line portion of stress-strain curves represents the elastic modulus (E).

Numerical values of E, plastic deformation and area under stress-strain curve (F) for the different polymer products are summarized in Table 4-12. Correlation between plastic deformation and toughness as estimated by area under the stress-strain curve is demonstrated in Fig. 4-25.

5.0 DISCUSSION

Some early results on accelerated radiation polymerization of MMA-TEGDMA comonomer mixtures (79) showed improved curing times and strength properties of the resulting polymer products. These preliminary experiments encouraged further systematic studies on radiation polymerization of vinyl-divinyl comonomer systems. Subsequently, the MMA-TEGDMA and S-TEGDMA comonomer systems were studied in detail over full concentration ranges of the mixtures (67,69,70). These results, briefly summarized as follows, served as the initial observations on which the present study was developed.

5.1 Radiation Polymerization of the MMA-TEGDMA Comonomer System

Radiation polymerization parameters for the MMA-TEGDMA system were derived at different comonomer compositions (vol/vol mixtures) from polymerization exotherm curves. These values obtained from bulk polymerizations are summarized in Tables 4-1 and 4-2. The accelerating ability of TEGDMA is illustrated over a wide concentration range by a hyperbolic decrease in t_{MAX} as shown in Fig. 4-1.

Pronounced acceleration accompanying TEGDMA addition as measured by t_{MAX} is primarily restricted to a narrow concentration interval . Additions of TEGDMA up to 10% are of

particular interest; amounts in excess of 10% are less effective. For example, addition of 10% TEGDMA to MMA decreased t_{MAX} from 117 min, for pure MMA, to 31 min. Further TEGDMA additions influenced t_{MAX} only moderately. The 50:50 comonomer composition, however, represented the most efficient mixture over the whole concentration range with t_{MAX} at only 15 min. Comonomer mixtures with higher concentration of crosslinking agent were less radiation sensitive. It is assumed that at high concentrations the crosslinking agent functions as a diffusion barrier limiting translocation of monomer to active radical sites.

The accelerating ability of TEGDMA as related to Ge may be expressed quantitatively by PRC as determined in "Activation" (PRC_I) and "Acceleration" (PRC_{II}) periods, i.e., before and after the onset of GEP, respectively. Both coefficients vary with composition of the comonomer mixture as shown in Fig. 4-2.

Up to 20% TEGDMA addition both coefficients increased very rapidly due to reduced termination in viscous and partly crosslinked media (43). Further increase in TEGDMA concentration affected not only the rate of termination, but also influenced the propagation rate. Both PRC_I and PRC_{II} became stabilized within the intermediate range of TEGDMA concentration (20-50%). In highly crosslinked systems, i.e., over 50% TEGDMA, chain growth propagation becomes fully diffusion-controlled; the reaction system was immobilized and consequently less

radiation sensitive. The dose required to obtain a solid copolymer with the 50:50 mixture was 0.2 Mrad (Table 4-2). Such a comonomer composition is 7.7 times more radiation sensitive than pure MMA.

The reciprocal of t_{MAX} ($1/t_{MAX}$) characterizes OCR /3-6/. From the relationship between OCR and TEGDMA concentration (Fig. 4-3), it is evident that for lower TEGDMA concentrations (up to 10%) OCR increased linearly. At higher TEGDMA concentrations OCR deviated from proportionality as accelerating efficiency decreased, possibly due to a diffusion barrier set in the more highly crosslinked networks. For concentrations falling within the proportionality range it was possible to predict the curing times of other mixtures according to the following empirical equation:

$$1/t_{MAX}\ (\text{mixture}) = 1/t_{MAX(MMA)} + K \cdot /DVM/ \quad \ldots\ldots\ldots /5\text{-}1/$$

where: /DVM/ = vol. concentration of TEGDMA, and

K = overall acceleration constant (OAC), slope as in Fig. 4-3.

Using this equation it is possible to predict required curing times within the most important concentration region. The proportionality constant (K) characterizes overall accelerating ability of a particular DVM or crosslinking agent. Its value for the MMA-TEGDMA system (0 to 10% TEGDMA) as

calculated from the linear portion of Fig. 4-3 is 1.1×10^{-3} $min^{-1} \cdot conc^{-1}$.

Deviation of OCR from the proportionality line within 10 to 20% TEGDMA concentration interval (Fig. 4-3) is in good agreement with results, derived from ESR studies by Szőcz and Lazar (100). They studied decay and segmental mobility of polymeric chains, as well as monomer molecules within crosslinked polyglycol methacrylate network.

For comonomer mixtures having higher densities of crosslinking, i.e., at higher TEGDMA concentrations, acceleration according to Ge has to be considered as the overall effect of two concurrent factors:

i. DVM acceleration resulting from decreased termination in the partly crosslinked network, and

ii. DVM retardation resulting from diffusion barriers and consequent diffusion-controlled propagation in highly crosslinked networks.

Gradual increases of TEGDMA up to 10% creates reaction conditions in which i predominates over ii. Additional increase in DVM concentration increasingly enlarges ii causing deviation of OCR from the proportionality line (Fig. 4-3).

5.2 Influence of Molecular Bridge Length in Divinyl Monomers

Crosslinking density of gelled MMA-DVM network depends on:

i. frequency of crosslinks on the polymer backbone i.e., poly(MMA), and
ii. molecular bridge length between DVM double bonds.

It seemed reasonable to assume that variation in DVM molecular bridge length would influence the DVM accelerating ability and affect the delay or premature onset of GEP. This hypothesis was tested with a series of dimethacrylate esters selected to act as crosslinking agents. Accelerating abilities of EGDMA, DEGDMA and TrEGDMA are given in Tables 4-3 and 4-4, while graphical interpretations of these results are illustrated in Fig. 4-4 and 4-5.

Changes in the accelerating ability of the different MMA-DVM systems studied, as shown by t_{MAX} in Fig. 4-4, indicate that accelerating ability changed according to DVM molecular bridge length. With increasing bridge length mono- (EGDMA), di (DEGDMA), tri- (TrEGDMA) to tetraethylene glycol dimethacrylate (TEGDMA) , t_{MAX} decreased over the whole concentration range studied. Acceleration by DVM in MMA-DVM mixtures is thus shown to be directly related to DVM molecular bridge length.

For example, at 2.5% DVM concentration t_{MAX} decreased from 83 min for MMA-EGDMA to 60 min for the MMA-TEGDMA comonomer system. Numerical t_{MAX} values for MMA-DEGDMA and MMA-TrEGDMA systems, at the same concentration, were 77 and 72 min, respectively. Similar results were obtained by evaluation of half-time concentration values, i.e., DVM concentrations required to reduce the curing time to one-half of that for pure MMA. Extrapolated values for half-time concentrations increased with decreasing DVM molecular bridge length. Such values for the four system studies were (Fig. 4-4):

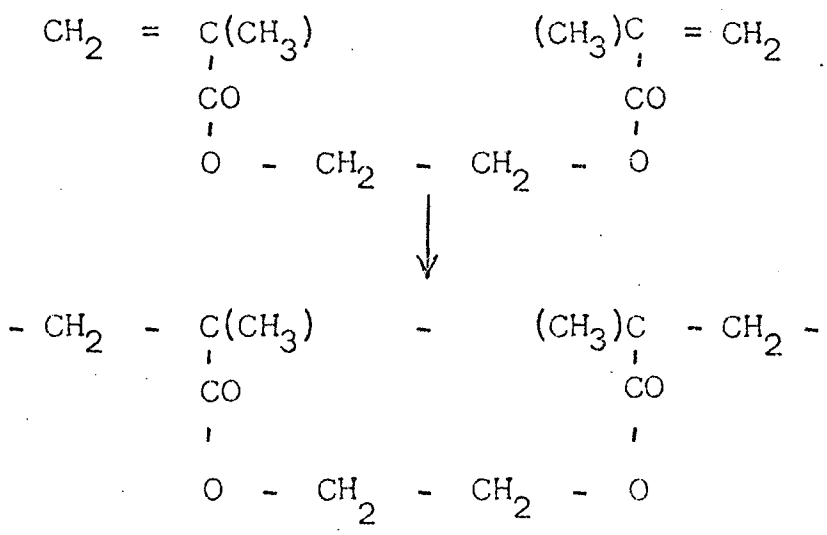
i. MMA-EGDMA 7%,
ii. MMA-DEGDMA 5%,
iii. MMA-TrEDGMA 4%, and
iv. MMA-TEGDMA 3%.

Comparison of half-time concentrations for the two extreme systems of this study (MMA-EGDMA and MMA-TEGDMA) shows that when EGDMA replaced TEGDMA, twice as much DVM was required to reduce t_{MAX} to one-half that for pure MMA. Higher EGDMA concentrations in the MMA-EGDMA system increased crosslinking density of the gelled network, creating diffusion barriers in the system. The propagation reaction is assumed to become diffusion-controlled at an earlier reaction stage for MMA-EGDMA than in the MMA-TEGDMA system. Consequently, t_{MAX} increases progressively.

Differences in crosslinking densities in these two systems can be demonstrated by the average segment molecular

weight between two crosslinks on the poly(MMA) backbone. For example, mixtures of 93:7 MMA-EGDMA and 97:3 MMA-TEGDMA represent comonomers of identical curing times, equalling one-half of that needed to cure MMA. However, the crosslink frequency is considerably higher in 93:7 MMA-EGDMA system in proportion to differences in DVM concentration and respective CN_{DVM}. The estimated average segment molecular weights between two crosslinks, assuming random distribution of DVM in the system, is nearly 10,000 for the 97:3 MMA-TEGDMA system, but in the 93:7 MMA-EGDMA system only 1,600-3,400 (based on MMA/DVM mole ratios given in Table 3-2). In addition the length of the molecular bridge between double bonds, which is four times longer in TEGDMA, assures higher segmental mobility and flexibility in the MMA-TEGDMA mixtures due to the numerous flexible C - O - C linkages (10). Additional substituents or branching of the molecular bridge increases the effective diffusion barrier and, consequently, t_{MAX}. This is also evident from lower accelerating ability of the trifunctional crosslinking agent used by Duran and Meyer (33), as demonstrated in Fig. 4-4.

Formation of ring structures arising from internal cyclization may also influence curing times. Considering EGDMA as an example, formation of the following ring structure is theoretically possible:



An additional ethylene glycol unit in the DVM molecular bridge results in enlargement of the ring size by three members. Thus, the 8-membered ring of EGDMA enlarges to 11-, 14-, and 17-membered rings for DEGDMA, TrEGDMA and TEGDMA, respectively.

The ring structures, surrounding active radical sites function as additional diffusion barriers. In addition, the internal linkage constitutes a loss of intermolecular bonding which would otherwise participate in crosslinking and gel formation. The overall result of both effects is delayed GEP and increased curing time. Formation of 6-membered rings is most favourable (59,78) and possibility of ring formation decreases with increasing ring size. This would explain the delay in onset of GEP for DVM studied in the sequence from TEGDMA to EGDMA, i.e., 23 to 41 min at 10% DVM concentration (Fig. 4-5 and Tables 4-1 and 4-3). Once GEP has been passed, formation of such internal links becomes progressively less

important as the distinction between internal and external links fades. Consequently, PRC_{II} is independent of the structure of DVM (Fig. 4-6) and t_{MAX} is directly proportional to t_{GEP} regardless of DVM molecular bridge length (Fig. 4-7). Similar conclusions were drawn from results on accelerated radiation polymerization of the S-TEGDMA comonomer system (70).

The formation of ring structures in DVM polymerizations has been proposed as a reason for poor correlation between predicted and actual gelation (38,40,48,91). Subsequently, proposed alternating inter-intra molecular propagation for these polymerization systems has been verified for a number of DVM (17,18,40). However, there is not enough direct evidence at this time supporting internal ring structures in studied crosslinked polymer products. Further structural analyses of copolymers may provide the necessary evidence to back up these contentions.

The relationshp between PRC_I and PRC_{II} at various DVM concentrations is indicated in Fig. 4-6. Both, PRC_I and PRC_{II} increased with increasing amount of DVM in the comonomer mixture over the concentration range studied (up to 30% DVM). Absolute PRC_{II} values at the same concentration level differed considerably from PRC_I values, as expected from two separate accelerating effects in the system studied:

i. acceleration by increased viscosity as represented by PRC_I, and

ii. acceleration by Ge as represented by PRC_{II}.

Numerical values of PRC_{II} are at least one order of magnitude higher than those of PRC_I (Tables 4-2 and 4-4). This is in a good agreement with rate constants observed before and after onset of GEP reported by Barthalemy (4). PRC_{II} was found to be independent of DVM structure, while PRC_I increased with initial viscosity of the comonomer mixtures, given in Table 3-2.

5.3 Prediction and Calculation of Curing Times

In previous studies (67,69) an empirical method was suggested for predicting curing times (t_{MAX}) for the MMA-TEGDMA comonomer system. The empirical equation /5-1/ was found to be valid for TEGDMA concentration up to 10% in the MMA-TEGDMA comonomer mixture. Application of /5-1/ to the present data derived for the MMA-DVM series, allows integration and comparison of previous data with results of the present study.

Mathematical treatment of data in Tables 4-1 and 4-3 gives the following OAC, as calculated from linear relationships between OAC and DVM concentration in Fig. 4-8:

$$\text{min}^{-1} \cdot \text{conc}^{-1}$$

i. $K_{MMA\text{-}EGDMA} = 1.1 \times 10^{-3}$

ii. $K_{MMA\text{-}DEGDMA} = 1.5 \times 10^{-3}$

iii. $K_{MMA\text{-}TrEGDMA} = 1.8 \times 10^{-3}$

iv. $K_{MMA\text{-}TEGDMA} = 2.4 \times 10^{-3}$

Numerical values of OAC for the different MMA-DVM systems demonstrate that accelerating ability increases with DVM molecular bridge length. As illustrated in Fig. 4-9 OAC values are inversely related to DVM connection number (CN_{DVM}). After calculation of CN_{DVM}, using /3-1/, one can estimate OAC from the following equation:

$$1/K_{MMA-DVM} = 5.2 \times CN_{DVM} - 10.55 \quad \ldots\ldots\ldots /5\text{-}2/$$

where: CN_{DVM} is connection number of respective DVM.

The linear relationship given by /5-2/ is illustrated in Fig. 4-9.

Relative accelerating ability of the DVM studied, expressed as OAC ratios with respect to the least effective in the series (EGDMA), increased as:

EGDMA : DEGDMA : TrEGDMA : TEGDMA = 1.0 : 1.36 : 1.64 : 2.18

Correlation of OAC with the DVM molecular bridge length is in good agreement with recent data on polymerization of dimethacrylate esters having variable bridge distances (8). Increase in absolute values of propagation constants (k_p) with molecular bridge length is demonstrated in Table 2-2.

From calculated OAC of individual comonomer systems it is possible to predict occurrence of maxima on polymerization exotherm curves. Differences in curing times (t_{MAX}) calculated from /5-1/, and those measured experimentally, are given in Table 4-5 for the four systems studied. These results demonstrate the usefulness of /5-1/, first derived for the MMA-TEGDMA system (67,69), later applied to the S-TEGDMA system (70) as recorded in Table 4-6. The equation can be applied to a variety of vinyl-divinyl comonomer systems. The average error for predicting curing times of the four systems studied was $\pm$ 5.7% (Table 4-5).

5.3.1 Application of the derived equation to published results

Kenaga (53) and recently Duran and Meyer (33) used the polymerization exotherm technique to evaluate the accelerating ability of various di- and trifunctional crosslinking agents polymerized by heat-catalyst systems. Both MMA (33) and styrene-type monomers (53) were polymerized in wood. Due to similarities between the conclusions of these authors and the implications of results from the present study, it was of interest to test applicability of Eq. /5-1/ to prediction of curing times from the data published.

Numerical values of OAC, calculated from Kenaga's data (53), were plotted against concentration of crosslinking agents. The expected linear relationships for these comonomer systems are given in Fig. 4-10. The following OAC values were

calculated for these systems:

$$\text{min}^{-1} \quad \text{conc.}^{-1}$$

i. $K_{TBS\text{-}TMPTMA} = 2.6 \times 10^{-4}$

ii. $K_{TBS\text{-}TrEGDMA} = 3.6 \times 10^{-4}$

iii. $K_{TBS\text{-}EGDMA} = 4.0 \times 10^{-4}$

iv. $K_{TBS\text{-}TEGDMA} = 4.8 \times 10^{-4}$

Only small differences were found between OAC of individual systems used by Kenaga (53). The reason for this may be the limited number of experiments carried out over the rather wide concentration range (only four experiments within the 0-30% concentration interval). However, OAC for all three di-functional crosslinking agents were higher than those calculated for the tri-functional TMPTMA. This suggests that substitution on the molecular bridge functions as a diffusion barrier for the propagation reaction.

Calculated OAC from data of Kenaga (53) were used to predict curing times for individual comonomer mixtures according to /5-1/. Differences in curing times (t_{MAX}) between calculated and published values are summarized in Table 4-7. Good agreement was found between actual and predicted values, regardless of differences in polymerization conditions and initiating system used. The average error of t_{MAX} was less than $\pm$ 5%.

Only two experiments have to be run in order to predict OAC. Expected curing times for different comonomer mixtures within concentration range covered by the two experiments can be calculated with the aid of /5-1/. This "two-point method" was tested by using experimental data published by Duran and Meyer (33). The following two experiments were randomly chosen:

i. comonomer composition, MMA:TMPTMA = 98:2; curing time, t_{MAX} = 108.3 min; and
ii. comonomer composition, MMA:TMPTMA = 91:9; curing time, t_{MAX} = 60.8 min.

Based on these two experiments, the calculated OAC value ($K_{MMA-TMPTMA} = 1.03 \times 10^{-3}$ min^{-1} conc.$^{-1}$) was used for predicting curing times of various MMA-TMPTMA compositions. Differences between calculated and published values (33) are summarized in Table 4-8. Agreement again, was quite good.

By integrating experimental results from this work with data already published, it is demonstrated that acceleration ability and curing times for different comonomer systems, regardless of the polymerization conditions, can be estimated within the most desirable practical concentration region by /5-1/ with a high level of confidence. From direct comparison of the respective OAC values it is apparent that all DVM studied were more effective accelerators than the trifunctional TMPTMA. This is graphically illustrated in Fig. 4-4 and 4-8.

A further disadvantage of trifunctional crosslinking agents is that they evolve more heat during the polymerization process. Peak temperature (T_{MAX}) increased very rapidly to 180-190 ^{o}C (33) which may be injurious to WPC. This could be avoided by lowering OCR if radiation is used as the energy source for polymerization. Data in Table 4-9 and Fig. 4-11 demonstrate that OCR varies linearly with the square root of radiation dose rate. At lower dose rates the temperature rises more gradually and T_{MAX} is considerably lower.

Another disadvantage of trifunctional crosslinking agents is their high tendency to develop diffusion barriers. Polymerization may cease due to lack of monomer diffusion in the highly crosslinked network. This problem is readily demonstrated with the MMA-TMPTMA system. For example, t_{MAX} at 15 and 20% TMPTMA in the system is essentially the same at 55 and 49.4 min, respectively. Conversion degree at these concentrations, however, decreased from 85.6% to 82.3% (33). In addition, trifunctional crosslinking agents form brittle polymer products with lower abrasion resistance (63). This was reported for WPC by Kenaga (53).

5.4 Analysis of Crosslinked Polymer Product Thermomechanical Curves

Thermomechanical properties of crosslinked polymer products depend primarily upon the tightness of the network

structure, i.e., crosslinking density caused by a given concentration of crosslinking agent. All DVM studied here functioned as efficient crosslinking agents and transformed linear and thermoplastic poly(MMA) to fully or partly crosslinked products. Linear, fully and partly crosslinked polymer products exhibit different thermomechanical curves as demonstrated in Fig. 3-2.

Crosslinking efficiency of individual DVM studied was not identical but varied with molecular bridge length. It increased according to the sequence:

$$\text{TEGDMA} < \text{TrEGDMA} < \text{DEGDMA} < \text{EGDMA}$$

This is demonstrated by shape of thermomechanical curves for copolymer products formed from the two DVM having extreme CN values, i.e., EGDMA with CN 2.200 (Fig. 4-12) and TEGDMA with CN 2.105 (Fig. 4-13).

Comparison of Fig. 4-12 and 4-13 shows that small additions of either DVM to MMA rapidly changed the linear poly(MMA) to a crosslinked thermoset plastic with increased network strength at higher temperatures. Transformation efficiency of EGDMA was, however, significantly higher.

Differences in crosslinking efficiency for these two DVM can be demonstrated by comparison of respective thermomechanical parameters as obtained at the same DVM concentration

level, as shown in Table 4-10. At 10% EGDMA in the MMA-EGDMA system, for example, T_g, TDD and TDT were 127 °C, 77% and 202 °C.

The same parameters for 10% TEGDMA in the MMA-TEGDMA system were considerably lower; T_g 113 °C, TDD 52% and TDT 165 °C. To obtain the same parameter values with TEGDMA, its concentration has to be increased to approximately 30% (Table 4-10 and Fig. 4-12 and 4-13).

Analysis of thermomechanical data for the four systems studied, Table 4-10, leads to the overall observation that increased DVM concentration influenced thermomechanical parameters in two ways:

i. increased T_g, TDT and TDD, and
ii. decreased LTDC.

T_g is an important parameter which is related to mobility of macromolecular segments (72,73). As expected, replacement of van der Waal's forces between polymer chains by carbon-carbon bonds reduced mobility of polymer segments and increased T_g. As illustrated in Fig. 4-14, it is possible to assess the contribution of DVM molecular bridge length to overall mobility of the crosslinked network in the four MMA-DVM systems studied. At the same crosslinking density (as expressed by copolymer CN) the shorter DVM bridge length gave lower segmental mobility and higher T_g (Fig. 4-14).

Stabilization of T_g at higher crosslinking densities (Fig. 4-14) can be interpreted by overlapping of two independent effects as related to T_g as:

i. crosslinking effect, and

ii. copolymerization effect.

The crosslinking effect always increases T_g, whereas the copolymerization effect decreases T_g. Both effects are additive (61). The crosslinking effect prevails at lower CN_{co}. At higher DVM concentration the contribution of the crosslinking effect is balanced by the copolymerization effect. The overall result is T_g stabilization (Fig. 4-14).

Resistance of individual polymer products to high temperature deformation can be expressed by TDD, while strength of the crosslinked network is proportional to TDT values. As demonstrated for the four stystems studied (Fig. 4-15), both parameters (TDD and TDT) are dependent on copolymer connection number (CN_{co}), regardless of the size of the molecular bridge of the crosslinking agent used. Both parameters increased rapidly within the narrow DVM concentration interval. Further addition of DVM to induce higher crosslinking densities changed TDD and TDT only moderately. This is an important observation and suggestively the effect coincides with both optimal acceleration and thermomechanical properties of polymer products at low DVM concentrations (compare Tables 4-3 and 4-10).

The linear thermomechanical deformation coefficient (LTDC) characterizes behaviour of heated polymer products within the transition region. LTDC represents the rate of polymer

deformation associated with the transition from plastic to rubbery state. Deformation of crosslinked polymer products in the rubbery region is constant across a broad temperature interval until the polymer loses coherence at temperatures equalling TDT (Fig. 3-2, 4-12 and 4-13).

It is to the advantage of crosslinked polymer products of the present study that LTDC decreased exponentially with DVM concentration in the system. This is demonstrated for the two system extremes (MMA-EGDMA and MMA-TEGDMA) using the semi-logarithmic plot in Fig. 4-16. Further, the relationship between LTDC and polymer crosslinking density as represented by copolymer connection number (CN_{CO}) can be used to great advantage in predicting thermomechanical behaviour of complex crosslinked polymer products derived from comonomer mixtures.

5.5 Analysis of Polymer Product Compression Stress-Strain Curves

Compression stress-strain curves were found to follow patterns represented by curves illustrated in Fig. 3-3. These show a wide variation in properties ranging from elastic, semi-rigid, hard, tough to brittle materials (20,72).

In general, soft and weak polymers (Fig. 3-3a) exhibit low modulus of elasticity (E), low yield point and moderate deformation at rupture. Hard and brittle materials show high E, no well-defined yield point and low deformation at rupture (Fig. 3-3b). Soft and tough plastics (Fig. 3-3c) show

low E and yield point but high deformation and rupture stress. Hard and strong plastics (Fig. 3-3d), on the other hand, exhibit high E and yield point but only moderate deformation. Finally, hard and tough materials (Fig. 3-3e) show E, yield point, deformation and rupture stress all to be high.

Typical compression stress-strain curves for the two extreme DVM systems studied over the full concentration range (MMA-EGDMA and MMA-TEGDMA), are reproduced in Fig. 4-18 and 4-19. Linear poly(MMA) exhibited compression stress-strain properties similar to those of poly(S) (20,70); i.e., it was hard and moderately tough (Fig. 3-3d). Highly crosslinked homopolymers of pure EGDMA (Fig. 4-18) and TEGDMA (Fig. 4-19) exhibited behaviour characteristic of hard and brittle polymers (Fig. 3-3b).

It was of particular interest to study shapes of compression stress-strain curves as obtained for the wide range of MMA-DVM comonomer mixtures. Experiments were concentrated within the most attractive concentration interval, i.e., up to 10% DVM in the respective comonomer systems. As shown in Tables 4-1 and 4-3 and Fig. 4-4, this region was of particular interest because of significantly accelerated curing. OCR within this concentration interval was proportional to DVM volume concentration (Fig. 4-8).

As demonstrated in Fig. 4-18 and 4-19, addition of EGDMA or TEGDMA to MMA caused change in shape of polymer compression stress-strain curves according to amount of DVM added.

They changed from hard and brittle-types (Fig. 3-3b) to hard and tough-types (Fig. 3-3e). These changes in stress-strain response indicate improvement in mechanical properties as follows:

i. rupture stress, plastic deformation and area under the stress-strain curve were much increased with 2.5 to 10% DVM addition to MMA,

ii. development of well-defined yield points at higher MMA concentration, and

iii. no significant change in slope of the initial Hookean portion occurred.

Numerical data of individual mechanical parameters, derived from compression stress-strain curves for the four MMA-DVM systems studied are summarized in Tables 4-11 and 4-12. Graphical interpretation of compression stress and strain at rupture and area under the stress-strain curve, as a function of comonomer composition for the four systems studied, are given in Fig. 4-20 through 4-23.

By comparison of the results compiled in Tables 4-11 and 4-12 the following observations can be made:

i. compression stress-strain properties of poly(MMA) with respect to rupture, yield and toughness parameters were higher than those of any DVM homopolymers studied;

ii. properties of products from comonomer mixtures

are not additive, i.e., the components do not contribute strength in proportion to their presence;

iii. compression stress and strain, as well as area under stress-strain curves, for all systems studied, exhibited well-defined maxima (Fig. 4-20 through 4-23);

iv. superior strength properties for the systems studied were restricted to the narrow concentration region, within 5 to 10% DVM in the system; and

v. the concentration interval showing superior strength properties broadened with increasing DVM molecular bridge length, i.e., in the sequence from EGDMA to TEGDMA.

Individual MMA-DVM systems differed only in specific details. Consider, as an example, location of the maxima on properties/composition curves (Fig. 4-20 through 4-23). They appeared at approximately 5% EGDMA concentration in the MMA-EGDMA system (Fig. 4-20). However, in the MMA-TEGDMA system the maxima were located near 10% TEGDMA concentration. It can be estimated from the respective MMA/DVM mole ratios, i.e., 34.3 for the MMA-EGDMA and 24.4 for the MMA-TEGDMA system (Table 3-2), that copolymers with superior strength properties possess approximately one crosslink for every 25 to 35 monomer units on the poly(MMA) backbone. Considering the MW of MMA to

be equal to 100, a number average molecular weight of 2,500 to 3,500 is obtained for poly(MMA) segments between two successive junctions. These values are in very good agreement with averages derived for crosslinked rubbers and thermoset copolymers (73), as calculated from swelling equilibria measurements.

From the limited differences in segmental MW between crosslinks, estimated for the two extreme comonomer systems studied, it was suggested that compression strength parameters can be related to comonomer connection number (CN_{co}). CN_{co} of individual copolymers, as calculated from /3-2/,are included in Table 4-11. Compression stress at rupture, as demonstrated in Fig. 4-24 for all four systems studied, is strongly related to CN_{co}, irrespective of the bridge length of crosslinking agent used. The crosslinking density of polymer networks as expressed by CN_{co} is a useful structural parameter. Although CN_{co} tells nothing about the configurational aspects of the crosslinked networks, it does quantitatively characterize resistance to both mechanical and thermomechanical deformations. Physical and thermomechanical properties of polymer products are assumed to be functions of crosslinking density as described by CN_{co}.

Observation of maxima at low DVM concentrations (Fig. 4-20 through 4-23) demonstrates an important discovery; that strength properties of solid crosslinked polymer products

vary with concentration of crosslinking agent in the same manner as strength properties of crosslinked rubbers and elstomers (28,29,32,35,37,63,94,102). For practical applications, a narrow DVM concentration interval (up to 10%) is the most attractive. Within this concentration range both maximum acceleration and superior mechanical and thermo-mechanical properties were obtained. Introduction of DVM with MMA within this range also rapidly increased the area under the compression stress-strain curve. The resulting copolymers are capable of considerable energy storage before failure. It was also observed that failure of these copolymers occurred with tremendous sound effects due to release of the energy stored.

In spite of the significance and importance of polymer toughness, standardized procedures for its evaluation are still lacking (72). From the observation that small stresses in the plastic range produced considerable deformation in tough polymer products (Fig. 4-18 and 4-19), it was assumed that plastic deformation is indicative of toughness. This is demonstrated by linear relationship between the area under the compression stress-strain curve and plastic deformation for the four systems studied in Fig. 4-25. Toughness of these copolymers seems to be independent of DVM molecular bridge length. A similar conclusion was reported for the S-TEGDMA comonomer system (70).

6.0 CONCLUSIONS

1. Acceleration in radiation polymerization of vinyl-divinyl comonomer systems *via* gel-effect (Ge) in crosslinked networks was related to the chemical structure of the crosslinking agents, in particular to their molecular bridge length. The overall curing rate (OCR) was found to be proportional to volume concentration of divinyl monomer (DVM). The overall acceleration constant (K) is inversely related to DVM connection number (CN_{DVM}) as:

$$1/K = 5.2 \times CN_{DVM} - 10.55$$

2. The relative acceleration ability of DVM studied increases with DVM molecular bridge length in the order: EGDMA : DEGDMA : TrEGDMA : TEGDMA = 1.00: 1.36 : 1.64 : 2.18. The half-time concentration values for EGDMA, DEGDMA, TrEGDMA and TEGDMA were approximately 7, 5, 4, and 3% (vol/vol), respectively.

3. Substantial decrease in curing time (t_{MAX}) was obtained with up to 10% DVM in the respective comonomer mixtures. Within this concentration interval superior mechanical and thermomechanical properties of copolymers were also observed.

4. The empirical equation for calculating the overall

acceleration constant and prediction of curing times was derived and applied to the four systems studied. Its extension to published results on acceleration in heat-catalyst systems was found to be fully applicable. Agreement between predicted and published results was within ±5% error for all copolymer systems observed.

5. Copolymer connection number (CN_{co}) was introduced and found to be a useful structural parameter for crosslinked copolymers. It characterizes and correlates quantitatively the mechanical and thermomechanical properties with copolymer crosslinking densities.

6. The MMA-TEGDMA comonomer system was found to be the most suitable and economically attractive. It represents a well balanced compromise of improved polymerization parameters and copolymer properties, suitable for wood-polymer composite products.

7.0 RECOMMENDATIONS FOR FURTHER STUDY

Based on theoretical considerations and experimental results of the present study the following are recommended as deserving of further research:

i. extend accelerated polymerization to the MMA-methyl acrylate system to examine influence of $-CH_3$ groups on Ge acceleration;

ii. extend the present MMA-DVM systems to higher homologous members (hexa-, deca-, etc., polyethylene glycol dimethacrylate) to examine effects of Ge onset and delayed diffusion-controlled propagation;

iii. examine structure of polymer products to collect evidence for possible internal ring formation;

iv. move from bulk copolymerization to accelerated polymerization within wood structures;

v. study the effect of a third component in the MMA-DVM system, for example to increase OCR in the presence of oxygen and/or to impart fire resistance properties (68);

vi. further extend utilization of exothermic heat as presently proposed for one-step production of veneer polymer overlaid plywoods (52,81).

8.0 LITERATURE CITED

1. Alfrey, T., Bohrer, J.J. and H. Mark. 1952. Copolymerization. IX. Copolymerization Involving Divinyl Monomers. Interscience Publ., New York. 269 pp.

2. Anon. 1970. Tentative method of test for compressive properties of rigid plastics. ASTM Standard D695-68T: 249-255.

3. Ballantine, D.S., Colombo, P., Glines, A. and B. Manowitz. 1954. The gamma-ray initiated copolymerization of styrene and methyl methacrylate. Chem. Eng. Proc. Symposium 50: 267-270.

4. Barthalemy, D.J. 1970. Radiolytic polymerization of methyl methacrylate in wood matrix. Heat transfer consideration. Ph.D. Thesis. Dissert. Abstr. University Microfilms Inc. 136 pp.

5. Beall, F.C., Meyer, J.A. and C. Skaar. 1966. Direct and R.F. heat curing of wood-plastic composites. Forest Prod. J. 16: 99-106.

6. Benson, S.W. and A.M. North. 1959. The effect of viscosity on the rate constants of polymerization reactions. J. Am. Chem. Soc. 81: 1339-1345.

7. Berlin, A.A. 1960. Synthesis and properties of polymethacrylates. Khimicheskaya Prom. 2: 14-20.

8. _____. 1969. About the influence of submolecular formation in liquid oligomers upon the kinetics of the formation, stereo-regularity and properties of space-crosslinked polymers formed from the oligomers. European Polymer J. Supl.: 15-41.

9. _____, Rodionova, Y.F. and V.Dabagova. 1953. Three dimensional polymerization of mixed allyl and carboxyallyl methacrylic esters. Zhurnal Obschei Khimii 2: 1560-1565.

10. Brice, T.G. and R.I. Coon. 1953. The effect of structure on the viscosities of perfluoroalkyl ethers and amines. J. Am. Chem. Soc. 75: 2921-2925.

11. Budyk, E. 1971. An introductory study of radiation polymerization of vinyl-divinyl systems. Unpbl. Rept., Fac. Forestry, Univ. B.C., Vancouver. 15 pp.

12. Burnett, G.M., Evans, P. and H.W. Melville. 1953. Polymerization of esters of methacrylic acids. Trans. Faraday Soc. 49: 1096-1107.

13. _____ and G.M. Duncan. 1962. High conversion polymerization of vinyl systems. I. Methyl methacrylate. Macromol. Chem. 51: 154-171.

14. _____. 1962. High conversion polymerization of vinyl systems. II. High methacrylates. Macromol. Chem. 51: 171-176.

15. _____. 1962. High conversion polymerization of vinyl systems. III. Methyl acrylate. Macromol. Chem. 51: 177-180.

16. _____ and H.W. Melville. 1946. Effect of environment on the reactivity of high polymers. Nature 186: 553-554.

17. Butler, G.B. 1967. The fundamental basis for cyclo-polymerization. Am. Chem. Soc., Div. Polymer Chem. Soc., Div. Polymer Chem., Preprints 8 (1): 35-38.

18. _____ and R.J. Angelo. 1957. Proposed alternating intramolecular-intermolecular chain propagation. J. Am. Chem. Soc. 79: 3128-3131.

19. _____ and F.L. Ingley. 1951. Preparation and polymerization of unsaturated quaternary amonium compounds. II. Halogenated allyl derivatives. J. Am. Chem. Soc. 73: 894-896.

20. Carswell, T.S. and H.K. Nason. 1944. Effect of environmental conditions on mechanical properties of organic plastics. Modern Plastics. 6: 41-44.

21. Cereza, R. 1962. Block and Graft Copolymers. Butterworth, London. 196 pp.

22. Chapiro, A. 1962. Radiation Chemistry of Polymeric Systems. High Polymer Series. Vol. 15. Interscience Publ., New York. 712 pp.

23. _____. 1969. Radical reactions in polymer gels and glasses. European Polymer J. Supl.: 43-54.

24. Charlesby, A. 1960. Atomic Radiation and Polymers. Pergamon Press, London. 556 pp.

25. Chen, C-p. In prep. Stress relaxation of paper plastic composites. Unpbl. M.Sc. Thesis, Fac. Forestry, Univ. B.C., Vancouver.

26. Cho, H.J. 1970. Differences in polymerization kinetics in and out of wood. Unpbl. Rept., Fac. Forestry, Univ. B.C., Vancouver. 13 pp.

27. _____. 1970. Gammacell calibration by Fricke dosimetry method. Unpbl. Progress Rept., Fac. Forestry, Univ. B.C., Vancouver. 7 pp.

28. Cooper, W. 1958. Copolymers of butadiene and unsaturated acids crosslinked by metal oxides. J. Polymer Sci. 28: 195-205.

29. Cuthrell, R.E. 1968. Epoxy polymers. II. Factors affecting the cure. J. Appl. Polymer Sci. 12: 955-967.

30. Czvikovsky, T. 1968. Wood plastic combinations. Atomic Energy Review, 4 (3). 99 pp.

31. Davies, A.G., Asbury, B.H. and C.G. Smith. 1969. Radiation polymerization kinetics in wood polymer preparation. Wood Sci. 2: 91-99.

32. Dudek, T.J. and F. Bueche. 1964. Tensile strength of gum and reinforced vulcanizates. J. Appl. Polymer Sci. 8: 555-564.

33. Duran, J.A. and J.A. Meyer. 1972. Exothermic heat released during catalytic polymerization of basswood methyl methacrylate composites. Wood Sci. Tech. 6: 59-66.

34. Flory, P.J. 1941. Molecular size distribution in three dimensional polymers. I. Gelation. J. Am. Chem. Soc. 63: 3083-3090.

35. _____. 1947. Effect of crosslinking and branching on the molecular constitution of diene polymers. J. Am. Chem. Soc. 69: 2893-2899.

36. _____. 1953. Principles of Polymer Chemistry. Cornell University Press, Ithaca. 672 pp.

37. Flory, P.J., Rabjohn, N. and M.C. Shaffer. 1949. Dependence of tensile strength of vulcanized rubber on degree of crosslinking. J. Polymer Sci. 4: 435-455.

38. Fox, T.G. and S. Loshaek. 1955. Influence of molecular weight and degree of crosslinking on the specific volume and glass temperature of polymers. J. Polymer Sci. 15: 371-390.

39. Glass, J.E. and N.L. Zutty. 1966. Investigation of autoacceleration effect during solution polymerization of styrene. J. Polymer Sci. 4(A): 1223-1243.

40. Gordon, M. and R.J. Roe. 1956. Diffusion and gelation in polyaddition. I. Classical network theory of gelation. J. Polymer Sci. 21: 27-37.

41. Ham, G.E. 1967. Vinyl Polymerization. Part I. Marcel Dekker, Inc., New York. 388 pp.

42. _____. 1969. Vinyl Polymerization. Part II. Marcel Dekker, Inc., New York. 416 pp.

43. Hayden, P. and H.W. Melville. 1960. The kinetics of the polymerization of methyl methacrylate. J. Polymer Sci. 43: 201-214.

44. Henderson, J.F., Grundy, K.H. and E. Fisher. 1968. Stress-birefringence properties of stryrene-isoprene block copolymers. J. Polymer Sci. 16(C): 3121-3131.

45. Holliday, L. 1968. The connection number of polymers with particular reference to carbon polymers. J. Appl. Polymer Sci. 12: 333-336.

46. _____ and W. A. Holmes-Walker. 1972. A new structural parameter of polymers. The relative number of network bonds per unit volume. J. Appl. Polymer Sci. 16: 139-155.

47. Holswoth, R.M. 1969. Application of thermal methods of analysis to organic coatings and related materials. J. Paint Tech. 41: 167-177.

48. Holt, T. and W. Simpson. 1956. Intermolecular reactions in addition polymerization systems. Proc. Roy. Soc. (London) 238(A): 154-174.

49. Huang, R.Y. and W.H. Rapson. 1963. Grafting onto cellulose by high energy radiation. J. Polymer Sci. 2(C): 169-188.

50. Huntsberger, D.V. 1967. Elements of Statistical Inference. Allyn & Bacon, Inc., Boston. 398 pp.

51. INSTRON. 1967. Manual No. 10-13-1 (D). Instron Co., Canton. 55 pp.

52. Kaneko, T. 1972. Radiation cured veneer plastic composites. Unpbl. Rept. WSI No. 72.2C, Fac. Forestry, Univ. B.C., Vancouver. 26 pp.

53. Kenaga, D.L. 1970. The heat cure of high boiling stryrene-type monomers in wood. Wood and Fiber 2: 50-60.

54. Kent, J.A., Winston, A. and W.R. Boyle. 1963. Preparation of wood plastic combinations using gamma radiation to induce polymerization. Rept. ORO 612, US AEC. 88 pp.

55. _____and L.Updyke. 1963. Manufacture of wood plastic combinations by use of gamma radiation. Industrial Uses of Large Radiation Sources. IAEC, Vienna. 404 pp.

56. _____, Loos, W.E. and J. E. Ayres. 1965. Preparation of wood plastic combinations using gamma radiation to induce polymerization. Rept. ORO 628, US AEC. 112 pp.

57. Korolev, G.V. and A. A. Berlin. 1962. The mechanism of autoacceleration in initial stages of polymerization of polyester-acrylates. Vysokomol. Soedinenya 4: 1654-1659.

58. _____ and T.Y. Kereli. 1962. The initial stage of polymerization of polyester-acrylates. Vysokomol. Soedinenya 4: 1520-1527.

59. Lenz, W.R. 1967. Organic Chemistry of Synthetic High Polymers. Interscience Publ., New York. 837 pp.

60. Lipscomb, N.T. and E.C. Weber. 1965. Kinetics of radiation induced low temperature polymerization of methyl methacrylate. J. Polymer Sci. 3: 55-61.

61. Loshaek, S. 1955. Crosslinked polymers. II. Glass temperatures of copolymers of methyl methacrylate and glycol dimethacrylates. J. Polymer Sci. 15: 391-401.

62. Majury, T.G. 1955. Polymerization of methyl methacrylate by pulses of high energy electrons. J. Polymer Sci. 15: 297-304.

63. Mark, H.F. 1965. Polymers in material science. J. Polymer Sci. 9(C): 1-33.

64. Matheson, M.S., Auer, E.E., Bevilacqua, E.B. and L.J. Hart. 1949. Rate constants in free radical polymerizations. I. Methyl methacrylate. J. Am. Chem. Soc. 71: 497-504.

65. _____. 1951. Rate constant in free radical polymerizations. IV. Methyl acrylate. J. Am. Chem. Soc. 73: 5395-5400.

66. Meyer, J.A. 1968. Crosslinking affects sanding properties of wood plastics. Forest Prod. J. 18: 89.

67. Micko, M.M. 1970. Radiation polymerization of liquid and solid comonomers. Unpbl. AECL Progress Rept. No. 5., WSI No. 70.7C., Fac. Forestry, Univ. B.C., Vancouver. 38 pp.

68. _____. 1971. Radiation polymerization of vinyl comonomer systems. Unpbl. AECL Progress Rept. No. 6., WSI No. 71.10 C., Fac. Forestry, Univ. B.C., Vancouver. 16 pp.

69. _____. 1971. Accelerated radiation polymerization of vinyl-divinyl comonomer systems. I. Methyl methacrylate- tetraethylene glycol dimethacrylate. Unpbl. Rept., Fac. Forestry, Univ. B.C., Vancouver. 36 pp.

70. _____. 1972. Accelerated radiation polymerization of vinyl-divinyl comonomer systems. II. Styrene-tetraethylene glycol dimethacrylate. Unpbl. Rept., Fac. Forestry, Univ. B.C., Vancouver. 60 pp.

71. _____, Wilson, J.W. and L. Paszner. In prep. Exothermic curves - a databank for control of vinyl monomer radiation polymerization.

72. Nielsen, E.L. 1965. Mechanical Properties of Polymers. Reinhold Publ. Co., London. 273 pp.

73. _____. 1970. Crosslinking effect on physical properties of polymers. Review in Macromolecular Chemistry. 4: 69-103.

74. Nikitina, T.S., Zhuravskaya, E.V. and A.S. Kuzminskij. 1963. Effect of Ionizing Radiation on High Polymers. Gordon & Breach, New York. 420 pp.

75. Norrish, R.G. and R.R. Smith. 1942. Catalyzed polymerization of methyl methacrylate in the liquid phase. Nature 150: 336-337.

76. Novikova, L.A., Dogadkin, S.A., Tarasova, N.Z. and A.S. Shaskov. 1968. Vulcanization of rubber with ethylene glycol bis-methacrylate. Vysokomol. Soedinenya 10(1): 211-215.

77. _____, Tarasova, N.Z. and S.A. Dogadkin. 1970. Vulcanization of rubber with glycol dimethacrylate esters having various molecular chain lengths. Vysokomol. Soedinenya (12(1): 63-68.

78. Odian, G. 1970. Principles of Polymerization. McGraw Hill Co., New York. 652 pp.

79. Paszner L. 1969. Radiation effects on wood products. Unpbl. AECL Progress Rept. No. 2, WSI No. 69.5C., Fac. Forestry, Univ. B.C., Vancouver. 27 pp.

80. _____. 1971. Radiation effects on wood products. Unpbl. AECL Progress Rept. No.5. WSI No. 70.7C., Fac. Forestry, Univ. B.C., Vancouver. 38 pp.

81. _____ and J.W. Wilson. 1971. Radiation cured veneer plastic composites. Unpbl. Rept. WSI No. 71.9 EA, Fac. Forestry, Univ. B.C., Vancouver. 16 pp.

82. Pesek, M., Jarkovsky, J. and F. Pultar. 1969. Radiation polymerization of methyl methacrylate in wood. Chemicky Prumysl 44: 503-506.

83. Rabinowitch, E. 1937. Collision, diffusion and reaction velocity in condensed systems. Trans. Faraday Soc. 33: 1225-1233.

84. Raff, R.A., Herrick, T.W. and M.F. Adams. 1965. Polymerization of styrene and styrene-divinyl benzene in wood. Forest Prod. J. 15: 260-262.

85. Ramalingam, K.V., Werezak, G.N. and J.W. Hodgins. 1963. Radiation induced graft polymerization of styrene in wood. J. Polymer Sci. 2(C): 153-157.

86. Riddle, E.H. 1954. Monomeric Acrylic Esters. Reinhold Publ. Co., New York. 524 pp.

87. Robertson, E.R. 1956. Diffusion control in the polymerization of methyl methacrylate and styrene. Trans. Faraday Soc. 52: 426-437.

88. Schildknecht, C.E. 1956. Polymer Processes. Vol. 10. Interscience Publ., New York. 915 pp.

89. Schulz, G.V. and G. Harborth. 1949. Über den Mechanismus des explosiven Polymerisations Verlaufes des Methacrylsauremethylesters. Macromol. Chem. 1: 106-139.

90. Siau, J.F., Meyer, J.A. and C. Skaar. 1956. Wood polymer combinations using radiation techniques. Forest Prod. J. 15: 425-434.

91. Simpson, W., Holt, T. and R.J. Zetie. 1953. The structure of branched polymers of diallyl phthalate. J. Polymer Sci. 10: 489-498.

92. _____ and T. Horton. 1955. Gelation in addition polymerization. J. Polymer Sci. 18: 335-349.

93. Singer, K.J. 1966. Wood plastic combinations prepared by gamma rays and high energy electrons. Symposium on Radiation Chemistry. Tihany, Hungary. pp. 715-726.

94. Smith, T.L. and A.B. Magnusson. 1960. Diisocyanate-linked polymers. II. Mechanical properties of some polyurethane elastomers. J. Polymer Sci. 42: 391-416.

95. _____ and R.A. Dickie. 1969. Viscoelastic and ultimate tensile properties of styrene-butadiene copolymers. J. Polymer Sci. 26(C): 163-187.

96. Stannet, V.T., Wellons, J. and H.J. Yasuda. 1963. Preparation and characterization of some cellulose graft copolymers. J. Polymer Sci. 4(C): 551-562.

97. Storey, B.T. 1965. Copolymerization of styrene and divinylbenzene. Initial rates of gel point. J. Polymer Sci. 3(A): 265-282.

98. Szymani, R. 1970. Testing of new radiation curable coatings for wood panelling. Unpbl. Rept., Fac. Forestry, Univ. B.C., Vancouver. 35 pp.

99. _____, Micko, M.M., Wilson, J.W. and L. Paszner. In prep. New radiation curable coatings.

100. Szőcz, F. and M. Lazar. 1969. ESR studies of free radicals in crosslinked polyglycol methacrylate. European Polymer J. Supl. 1969: 337-343.

101. Taneda, K., Hasagava, I. and H. Kawakami. 1970. Dependence of the rule of mixture about mechanical properties of wood plastic composites. J. Japan Wood Res. Soc. 17: 181-187.

102. Taylor, G.R. and S.R. Darin. 1955. The tensile strength of elastomers. J. Polymer Sci. 17: 511-525.

103. Trommsdorff, V.E., Kohle, H. and P. Lagally. 1948. Zur Polymerisation des Methacrylsauremethylesters. Macromol. Chem. 1: 168-198.

104. Vaughan, M.F. 1952. Diffusion controlled reactions during the bulk polymerization of styrene. Trans. Faraday Soc. 48: 576-579.

105. Walling, C. 1945. Gel formation in addition polymerization. J. Am. Chem. Soc. 67: 441-447.

106. _____. 1957. Free Radicals in Solution. John Willey, New York. 631 pp.

Table 2-1. Effect of conversion level on polymerization characteristics of methyl methacrylate (MMA) at 22.5°C (43).

Conversion, %	R_p, %/hr	k_p	$k_t \times 10^{-5}$	$(k_p/k_t^{1/2}) \times 10^2$
0	3.5	384	442	5.78
10	2.7	234	273	4.58
20	6.0	267	72.6	8.81
30	15.4	303	14.2	25.60
40	23.4	368	8.93	38.90
50	24.5	258	4.03	40.60
60	20.0	74	0.498	33.20
70	13.1	16	0.0564	21.30
80	2.8	1	0.0076	3.95

Table 2-2. Some data on polymerization of dimethacrylatic esters (photoinitiator-benzoin 0.2%) (8).

N	The compound	Symbol	$\bar{M}_n$	Viscosity c.p.	The degree of transformation (%)	The temperature of polymerization	$\frac{W}{\bar{M}} 10^5$ (sec^{-1})	K_p l. $mole^{-1} sec^{-1}$	K_t l. $mole^{-1}$ sec
1	Methylmethacrylate	MMA	100	50	50	25	0·2	—	—
2	Dimethacrylate of butyleneglycol	MB	226	4·0	0	25	3·8	600	8.10^5
3	Dimethacrylate of butyleneglycol	MB	226	—	30	25	4·0	112	$2·3.10^4$
4	Dimethacrylate of butyleneglycol	MB	226	—	5	25	33·0	17	83.10^2
5	Dimethacrylatehexa-methyleneglycol	MG	244	4·9	0	25	13·0	1200	$6·2.10^5$
6	Dimethacrylatehexa-methyleneglycol	MG	244	—	5	25	7·0	245	$3·7.10^4$
7	Dimethacrylatehexa-methyleneglycol	MG	244	—	30	25	4·0	26	$1·3.10^3$
8	Dimethacrylatedeca-methyleneglycol	MD	300	7·7	0	25	16·0	1880	$4·2.10^5$
9	Dimethacrylatedeca-methyleneglycol	MD	300	—	5	25	24·0	1400	$1·5.10^5$
10	Dimethacrylatedeca-methyleneglycol	MD	300	—	30	25	29·0	840	$2·5.10^4$
11	Dimethacrylate (*bis*-diethyleneglycol) phthalote	MGPh	566	51·0	0	30·6	20·0	2470	$4·8.10^5$
12	Dimethacrylate (*bis*-diethyleneglycol) phthalote)	MGPh	566	—	5	30·6	24·0	2300	$2·7.10^5$
13	Dimethacrylate (*bis*-diethyleneglycol) phthalote	MGPh	566	—	30	30·6	54·0	1750	$3·2.10^4$

Notes: (1) For MMA at $\alpha = 0$ per cent $K_p = 300$ l. $mole^{-1}$ sec^{-1} ($T = 25°$).
(2) The kinetics of polymerization of MB, MG, MD, MGF were studied by methods of precision dilatometry and thermometry.

Table 3-1. Some properties of methyl methacrylate (MMA) and divinyl monomers (DVM) used in this study.

Name, (abr.) formula	n	Mw	d, g/cm^3	CN	η_{rel} 25°C
Methyl methacrylate, (MMA) $C_5H_9O_2$	--	100	0.940	2.000	1.0
Ethylene glycol dimethacrylate, (EGDMA) $C_{10}H_{14}O_4$	1	198	1.045	2.200	4.2
Diethylene glycol dimethacrylate, (DEGDMA) $C_{12}H_{18}O_5$	2	242	1.062	2.150	6.9
Triethylene glycol dimethacrylate, (TrEGDMA) $C_{14}H_{22}O_6$	3	286	1.090	2.125	10.5
Tetraethylene glycol dimethacrylate, (TEGDMA) $C_{16}H_{26}O_7$	4	330	1.140	2.105	28.4

Table 3-2. Concentrations and relative viscosities of different methyl methacrylate (MMA)-divinyl monomer (DVM) mixtures.

DVM	DVM fraction in comonomer mixture		Mole ratios		η_{rel}
	volume	mole	DVM/MMAx10	MMA/DVM	25° C
EGDMA	0.025	0.013	0.14	70.5	1.04
	0.050	0.028	0.29	34.3	1.08
	0.100	0.059	0.63	15.9	1.14
	0.150	0.087	1.00	10.0	1.24
	0.200	0.123	1.40	7.1	1.33
	0.300	0.194	2.40	4.2	1.41
DEGDMA	0.025	0.012	0.13	83.5	1.05
	0.050	0.024	0.25	40.5	1.11
	0.100	0.049	0.52	19.2	1.18
	0.150	0.077	0.83	12.0	1.27
	0.200	0.104	1.16	8.6	1.34
	0.300	0.167	2.00	5.0	1.55
TrEGDMA	0.025	0.011	0.12	85.4	1.08
	0.050	0.020	0.21	47.0	1.20
	0.100	0.043	0.45	22.2	1.28
	0.150	0.065	0.69	14.4	1.42
	0.200	0.092	1.01	9.9	1.53
	0.300	0.144	1.69	5.9	1.83
TEGDMA	0.025	0.009	0.09	102.0	1.14
	0.050	0.019	0.19	57.8	1.29
	0.100	0.039	0.41	24.4	1.48
	0.300	0.138	1.88	5.3	2.54

Table 4-1. Polymerization exotherm characteristics for the MMA-TEGDMA comonomer system (67,69).

Comonomer composition, vol. %		Gel-Effect Point (GEP)		MAX	
MMA	TEGDMA	t_{GEP}, min	T_{GEP}, °C	t_{MAX}, min	T_{MAX}, °C
100	0	106	62	117	120
97.5	2.5	52	69	60	159
95	5	30	60	45	160
90	10	23	57	31	167
70	30	14	54	20	165
50	50	10	53	15	157
30	70	13	57	18	149
0	100	16	61	22	130

Table 4-2. Calculated polymerization parameters for the MMA-TEGDMA comonomer system (67,69).

Comonomer Composition, vol %		Exotherm peak parameters		Polymerization Rate Coefficient (PRC), °C/min		PRC_{II}/PRC_I
MMA	TEGDMA	Dose, Mrad	ΔT, °C	PRC_I	PRC_{II}	
100	0	1.50	84	0.24	5.2	21.6
95.5	2.5	0.81	123	0.64	5.0	7.9
95	5	0.61	124	0.80	6.7	8.4
90	10	0.42	131	0.91	13.8	15.2
70	30	0.27	129	1.28	18.3	14.3
50	50	0.20	121	1.64	20.0	12.7
30	70	0.24	111	1.60	16.7	9.8
0	100	0.30	94	1.56	11.5	7.3

Table 4-3. Polymerization exotherm characteristics for MMA-EGDMA, MMA-DEGDMA and MMA-TrEGDMA comonomer systems.

DVM	Comonomer composition, vol %		Gel-Effect Point (GEP)		MAX	
	MMA	DVM	t_{GEP}, min	T_{GEP}, °C	t_{MAX}, min	T_{MAX}, °C
EGDMA	97.5	2.5	69	68	83	149
	95	5	55	62	66	156
	90	10	41	57	50	171
	85	15	34	57	41	174
	80	20	30	56	37	176
	70	30	25	59	31	176
	0	100	21	52	37	114
DEGDMA	97.5	2.5	64	66	77	156
	95	5	50	64	61	164
	90	10	28	59	39	176
	85	15	25	58	33	178
	80	20	23	56	29	176
	70	30	21	60	27	179
	0	100	18	56	30	128
TrEGDMA	97.5	2.5	59	68	72	154
	95	5	44	64	54	160
	90	10	27	57	36	174
	85	15	22	56	29	174
	80	20	20	56	27	184
	70	30	18	56	24	175
	0	100	18	57	28	127

Table 4-4. Calculated polymerization parameters for MMA-EGDMA, MMA-DEGDMA and MMA-TrEGDMA comonomer systems.

DVM	Comonomer composition, vol %		Exotherm peak parameters		Polymerization Rate Coefficient(PRC), °C/min		PRC_{II}/PRC_{I}
	MMA	DVM	Dose, Mrad	ΔT, °C	PRC_{I}	PRC_{II}	
EGDMA	97.5	2.5	0.91	113	0.46	5.8	12.2
	95	5	0.73	120	0.47	8.5	18.1
	90	10	0.55	135	0.51	12.6	24.8
	85	15	0.45	138	0.62	16.7	26.9
	80	20	0.39	140	0.66	17.1	25.8
	70	30	0.34	140	0.92	19.5	21.2
	0	100	0.39	78	0.76	3.9	5.1
DEGDMA	97.5	2.5	0.85	120	0.53	6.9	13.0
	95	5	0.67	128	0.56	9.1	16.2
	90	10	0.43	140	0.80	11.7	14.7
	85	15	0.36	142	0.88	17.2	19.5
	80	20	0.32	140	0.90	15.0	16.6
	70	30	0.30	143	1.10	19.8	18.0
	0	100	0.33	92	1.11	6.0	5.4
TrEGDMA	97.5	2.5	0.79	118	0.54	6.6	12.2
	95	5	0.59	124	0.64	9.6	13.5
	90	10	0.39	138	0.77	13.0	16.9
	85	15	0.32	138	0.91	16.9	18.5
	80	20	0.30	146	1.00	18.0	18.0
	70	30	0.26	139	1.20	19.0	15.8
	0	100	0.31	91	1.16	7.0	6.0

Table 4-5. Differences between measured and calculated curing times for lower concentrations of divinyl monomer (DVM) in MMA-DVM systems.

DVM	Comonomer composition, vol %		t_{MAX}, min		Difference	
	MMA	DVM	calculated	measured	min	%
EGDMA	97.5	2.5	88	83	+5	+6.0
	95	5	70	66	+4	+6.1
	90	10	49	50	-1	-2.0
	85	15	38	41	-3	-7.3
DEGDMA	97.5	2.5	81	77	+4	+4.9
	95	5	62	61	+1	+1.6
	90	10	42	39	+3	+7.1
	85	15	31	33	-2	-6.5
TrEGDMA	97.5	2.5	76	72	+4	+5.5
	95	5	56	54	+2	+3.7
	90	10	37	36	+1	+2.8
	85	15	27	29	-2	-6.9
TEGDMA	97.5	2.5	68	60	+8	+13.5
	95	5	48	45	+3	+6.7
	90	10	30	31	-1	-3.3
						*±5.7

*An average error for predicting curing time for the four systems studied.

Table 4-6. Differences between measured and calculated curing times for lower concentrations of TEGDMA in the styrene (S)-TEGDMA system (70).

Comonomer composition, vol %		t_{MAX}, min		Difference	
S	TEGDMA	calculated	measured	min	%
95	5	887	822	+55	+6.5
90	10	445	462	-17	-3.8
80	20	222	228	-6	-2.6
80	20	222	222	0	0.0
70	30	148	135	+13	+9.6
60	40	110	97	+13	+13.2
50	50	69	87	-18	-20.6

Table 4-7. Differences in calculated and published curing times for TBS - di- and tri-vinyl comonomer systems (53).

Crosslinking monomer		t_{MAX}, min		Difference	
type	%	measured	calculated	min	%
EGDMA	5	52	53	+1	+1.9
	10	46	48	+2	+4.3
	20	40	40	0	0
	30	34	35	+1	+3.1
TrEGDMA	5	36	36	0	0
	10	34	34	0	0
	20	30	30	0	0
	30	27	27	0	0
TEGDMA	5	40	41	+1	+2.5
	10	35	37	+2	+5.7
	20	34	32	-2	-5.9
	30	27	28	+1	+3.7
TMPTMA	5	50	49	-1	-2.1
	10	48	46	-2	-4.2
	20	40	42	+2	+5.0
	30	37	37	0	0

Table 4-8. Differences in calculated and published curing times for heat-catalyst cured MMA - trimethylol propane trimethacrylate (TMPTMA) polymerization system (33).

TMPTMA,	t_{MAX}, min		Differences	
%	calculated	measured	min	%
1	123.0	123.4	-0.4	-0.3
2*	108.3	108.3	0.0	0.0
5	81.5	81.3	+0.2	+0.3
7	69.8	72.5	-2.7	-3.7
9*	60.8	60.8	0.0	0.0
12	51.3	55.5	-4.2	-7.6

* Values used for calculation of overall acceleration constant by "two-point method."

Table 4-9. Radiation polymerization of TEGDMA at different dose rates.

Dose rate		MAX		$1/t_{MAX} \times 10^2$
rad/sec	$(rad/sec)^{1/2}$	t_{MAX}, min	T_{MAX}, °C	
220	14.8	22	130	4.55
202	14.1	31	107	3.22
156	12.5	89	88	1.12

Table 4-10. Thermomechanical properties of radiation cured poly(MMA) and crosslinked MMA-DVM polymer products.

Monomer	Comonomer Composition, vol %		CN_{co}	LTDCx10^4, 1/°C	T_g, °C	TDD, %	TDT, °C
	MMA	DVM					
MMA	100	0	2.000	551	108	0	125
EGDMA	97.5	2.5	2.003	388	115	49	175
	95	5	2.006	302	123	60	198
	90	10	2.012	125	127	77	202
	70	30	2.039	15	130	92	214
	50	50	2.072	4	130	94	250*
DEGDMA	97.5	2.5	2.002	437	114	41	158
	95	5	2.004	350	115	46	164
	90	10	2.007	263	119	61	175
	70	30	2.025	82	122	82	200
	50	50	2.048	21	125	87	198
TrEGDMA	97.5	2.5	2.001	476	111	25	155
	95	5	2.003	375	113	50	165
	90	10	2.005	275	116	63	180
	70	30	2.018	102	119	83	195
	50	50	2.036	57	122	92	207
TEGDMA	95	5	2.002	425	110	37	160
	90	10	2.004	326	113	52	165
	85	15	2.007	275	115	61	185
	70	30	2.014	126	117	81	203
	50	50	2.029	68	117	88	197

*Over 250 °C, maximum for equipment

Table 4-11. Mechanical properties of radiation cured poly (MMA) and crosslinked MMA-DVM polymer products.

Monomer	Comonomer composition, vol. %		CN_{co}	YIELD		RUPTURE	
	MMA	DVM		STRESS, kg/cm^2	STRAIN, %	STRESS, kg/cm^2	STRAIN, %
MMA	100	0	2.000	1,080	6.0	2,100	50.5
EGDMA	97.5	2.5	2.003	1,080	7.0	4,450	62.2
	95	5	2.006	1,060	6.7	4,770	67.5
	90	10	2.012	1,080	7.0	3,950	55.0
	80	20	2.024	1,020	6.0	2,550	38.5
	50	50	2.072	955	5.0	1,530	20.0
	40	60	2.092	---	---	1,330	17.5
	20	80	2.138	---	---	1,210	12.5
	0	100	2.200	---	---	895	5.5
DEGDMA	97.5	2.5	2.002	1,150	7.5	3,915	60.5
	95	5	2.004	1,050	7.0	4,680	65.5
	90	10	2.007	1,050	7.0	3,950	54.0
	70	30	2.025	1,050	6.5	2,770	42.5
	50	50	2.048	1,020	6.0	1,910	27.0
	20	80	2.099	895	5.5	1,400	15.0
	0	100	2.150	---	---	825	5.5
TrEGDMA	97.5	2.5	2.001	1,020	7.0	3,630	63.0
	95	5	2.003	1,050	7.5	4,650	66.0
	90	10	2.005	1,020	7.6	4,580	62.5
	70	30	2.018	1,000	7.0	3,120	48.0
	60	40	2.026	960	6.5	2,510	44.5
	50	50	2.036	950	6.0	2,230	36.0
	30	70	2.061	950	5.5	1,520	20.0
	0	100	2.125	---	---	1,250	11.5
TEGDMA	95.5	2.5	2.001	925	6.0	4,710	67.0
	95	5	2.002	955	6.5	5,100	68.5
	90	10	2.004	1,080	7.0	5,030	67.0
	70	30	2.014	1,050	7.0	3,890	59.5
	50	50	2.029	955	7.0	2,450	47.0
	40	60	2.037	860	6.0	2,250	41.0
	20	80	2.062	765	5.0	1,520	27.0
	0	100	2.105	510	2.5	1,660	26.5

Table 4-12. Calculated parameters from compression stress-strain curves for radiation cured poly (MMA) and MMA-DVM polymer products.

Monomer	Comonomer composition, vol. %		E, $kg/cm^2 x10^{-3}$	Plastic Deformation, %	F, cm^2
	MMA	DVM			
MMA	100	0	19.0	44.5	32.3
EGDMA	97.5	2.5	20.0	55.0	49.5
	95	5	19.0	61.0	55.7
	90	10	19.0	48.0	45.8
	80	20	19.0	32.5	27.8
	50	50	18.5	15.0	11.1
	40	60	18.0	----	6.8
	20	80	18.0	----	6.1
	0	100	16.5	----	1.0
DEGDMA	97.5	2.5	19.0	53.0	50.9
	95	5	19.5	58.5	56.6
	90	10	19.0	44.0	48.1
	70	30	18.0	36.0	30.4
	50	50	18.0	21.0	17.1
	20	80	17.0	9.5	7.3
	0	100	17.0	----	1.5
TrEGDMA	97.5	2.5	18.0	56.0	47.5
	95	5	19.5	58.5	56.5
	90	10	20.0	55.0	54.1
	70	30	17.0	41.0	34.8
	60	40	16.5	38.0	26.6
	50	50	17.0	30.0	23.3
	30	70	17.0	14.5	10.9
	0	100	17.0	----	7.7
TEGDMA	97.5	2.5	18.5	61.0	55.6
	95	5	18.5	62.0	59.5
	90	10	20.0	60.0	57.5
	70	30	19.5	52.5	49.4
	50	50	17.0	40.0	34.8
	40	60	16.0	35.0	25.3
	20	80	15.0	22.0	14.5
	0	100	15.0	24.0	13.9

Figure 3-1. Solution of a typical polymerization exotherm curve including derivation of "Gel-Effect Point" (GEP), "Cure" (MAX), and showing "Activation" (I) and "Acceleration" (II) periods (67,69,71).

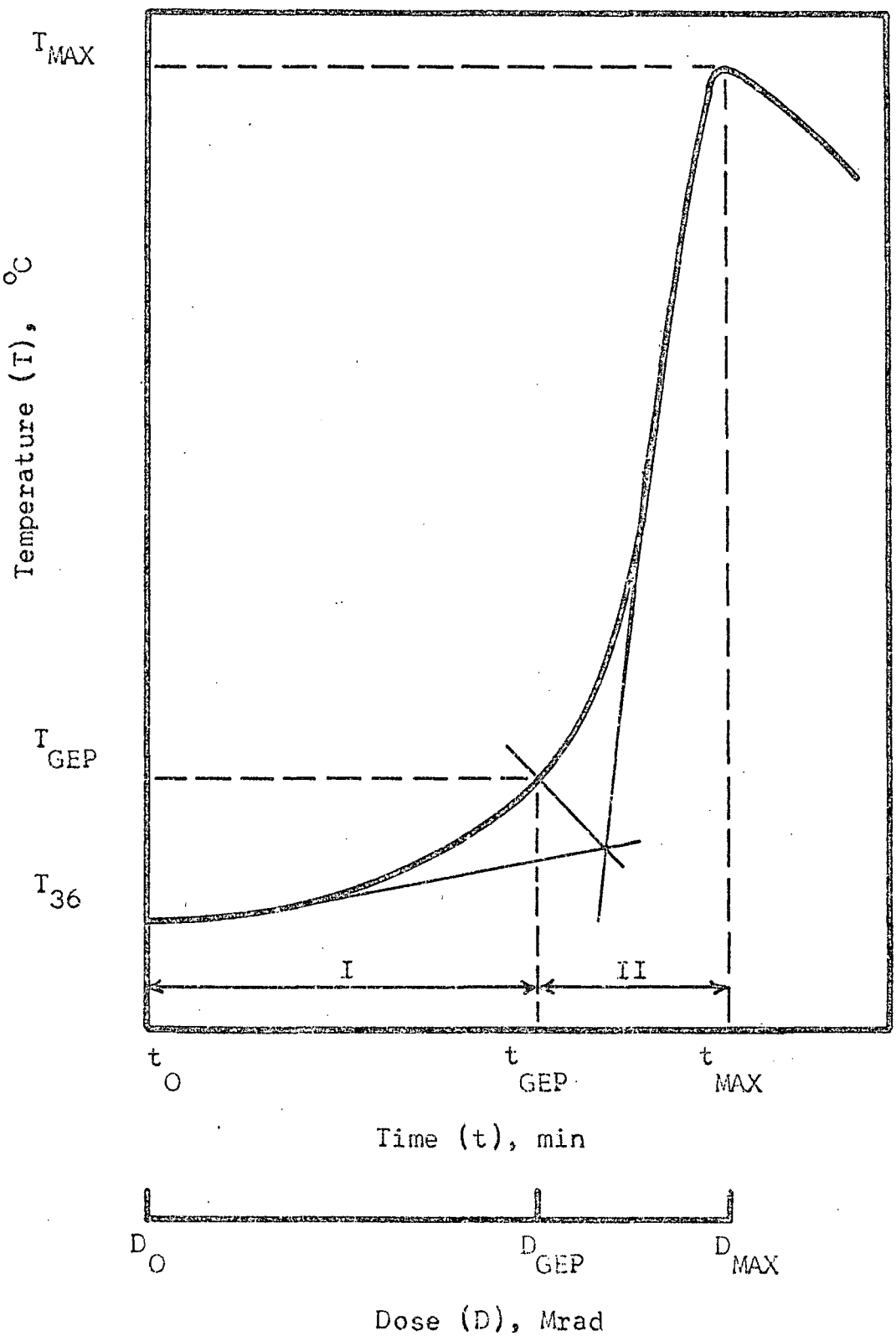


Figure 3-2. Typical thermomechanical curves for thermoplastic (1), partly crosslinked (2) and fully crosslinked (3) polymer products; and showing for (2) solutions for glass transition temperature (T_g), thermal distortion temperature (TDT) and slope (s) in the transition region (67,69).

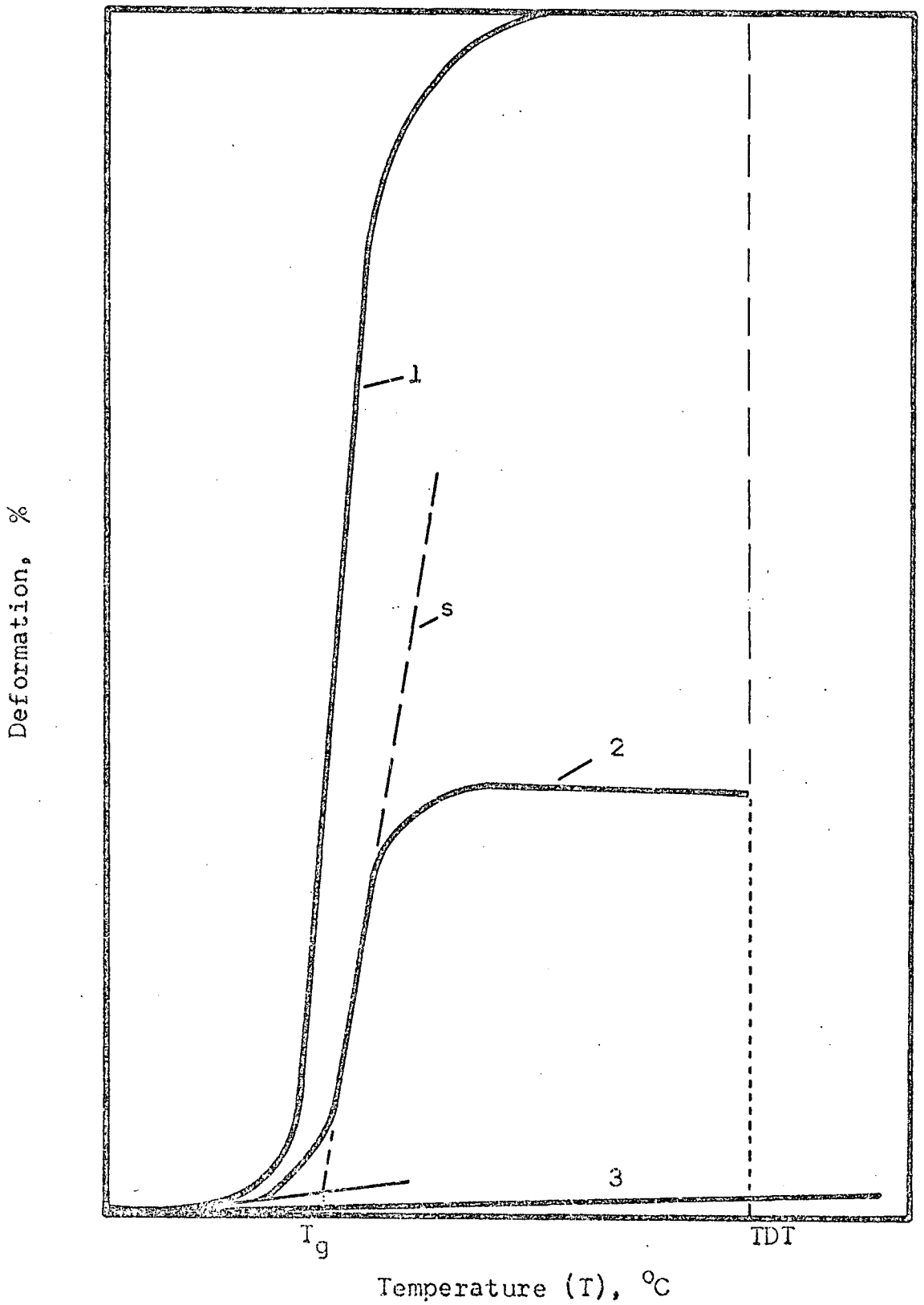


Figure 3-3. Polymer stress-strain curve nomenclature and typical curves for different types of plastics (20,72).

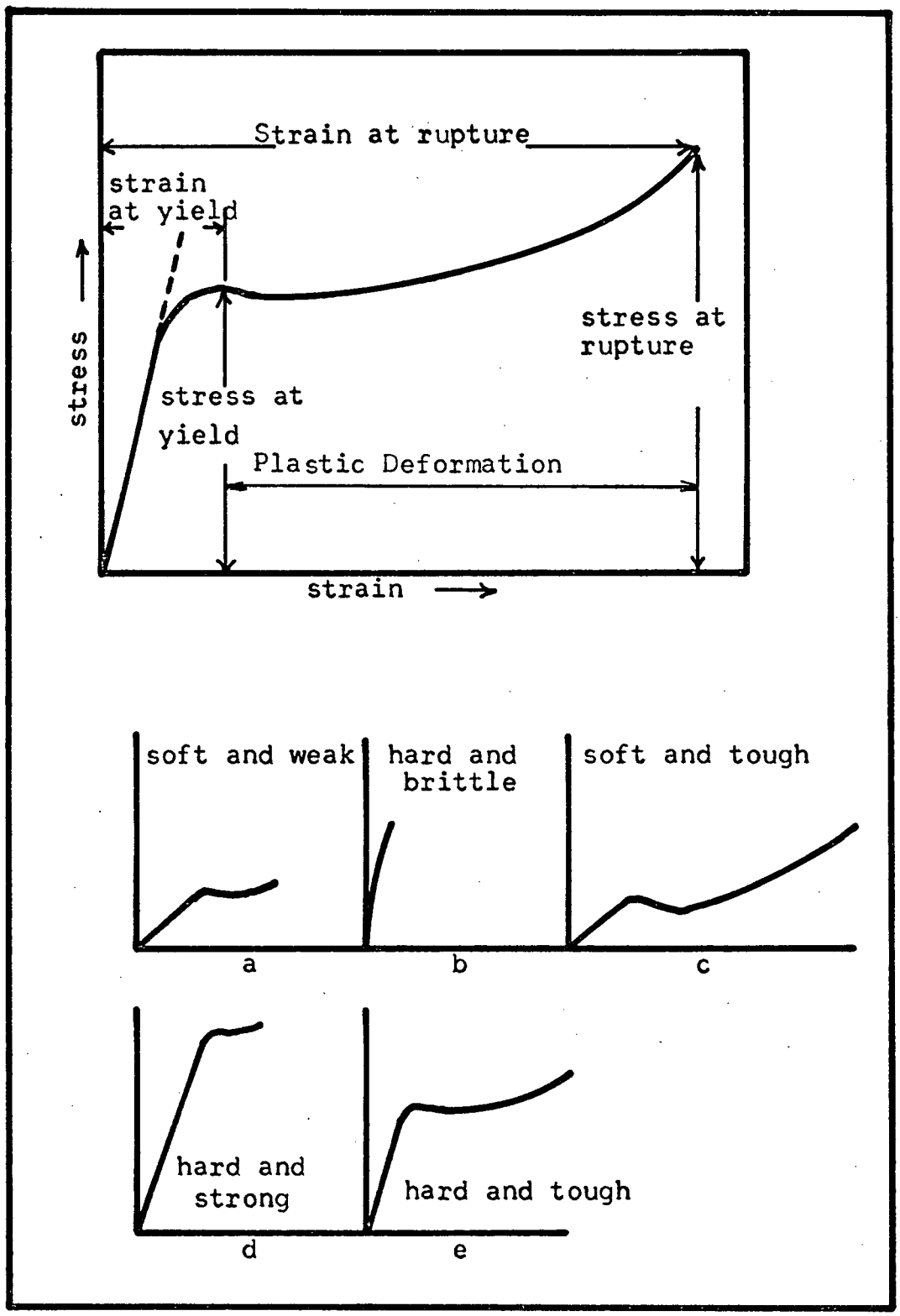


Figure 4-1. Relationship between t_{MAX} and volume concentration of TEGDMA in the MMA-TEGDMA comonomer mixture (67,69).

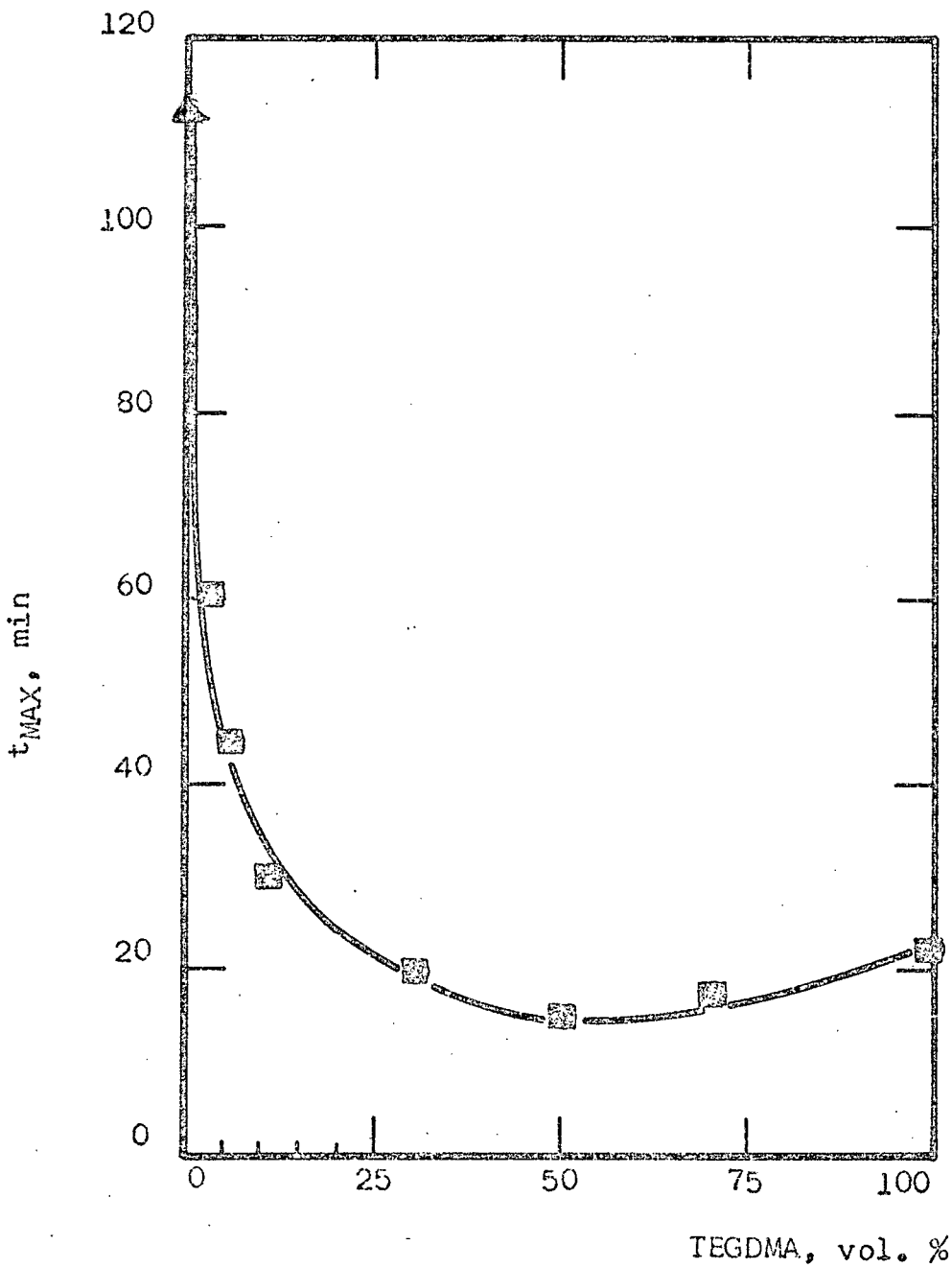


Figure 4-2. Polymerization rate coefficients in "Activation" (PRC_I) and "Acceleration" (PRC_{II}) periods as functions of TEGDMA volume concentration in the MMA-TEGDMA comonomer mixture (67,69).

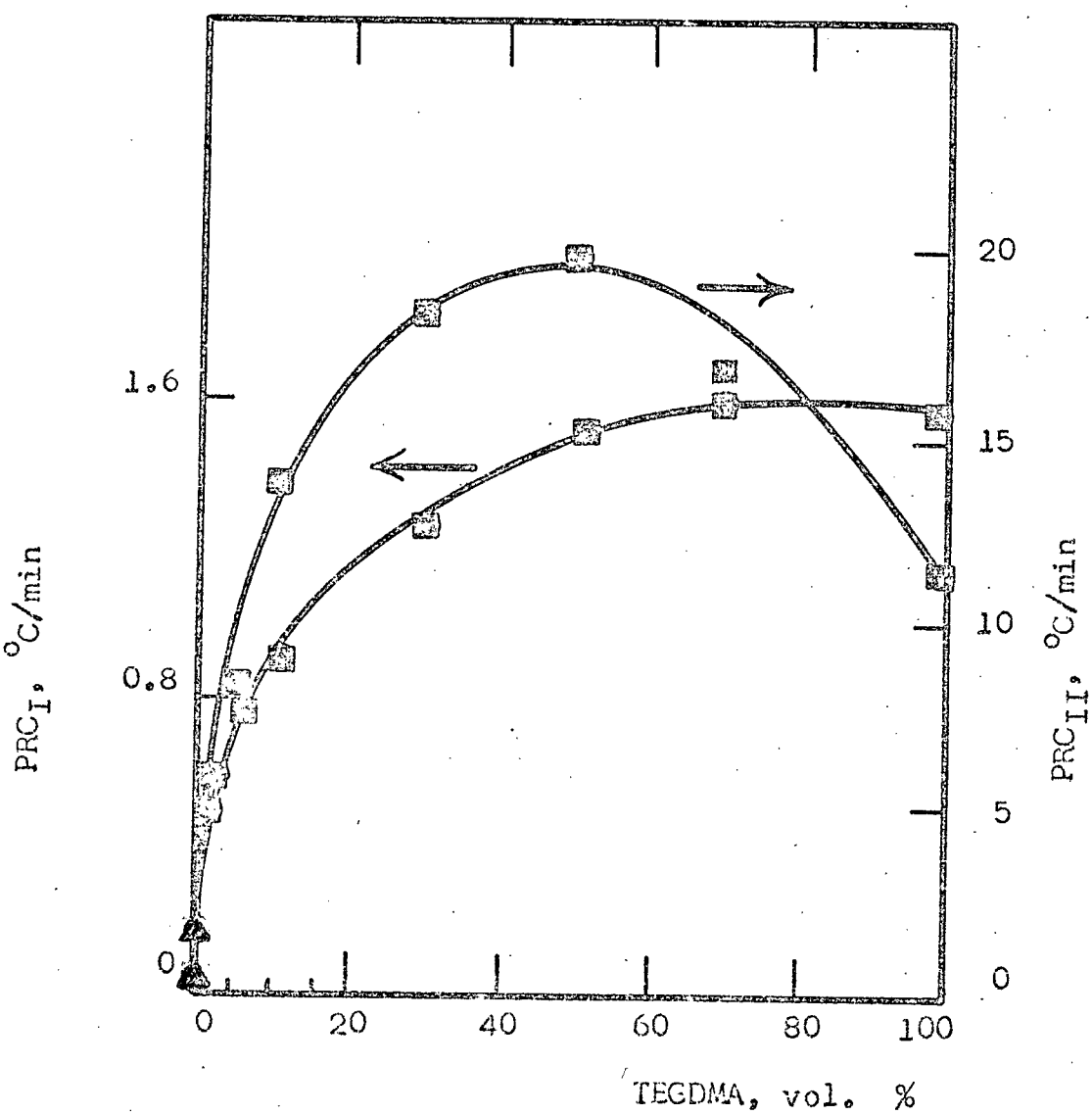


Figure 4-3. Relationship between overall curing rate ($1/t_{MAX}$) and TEGDMA volume concentration in the MMA-TEGDMA comonomer mixture (67,69).

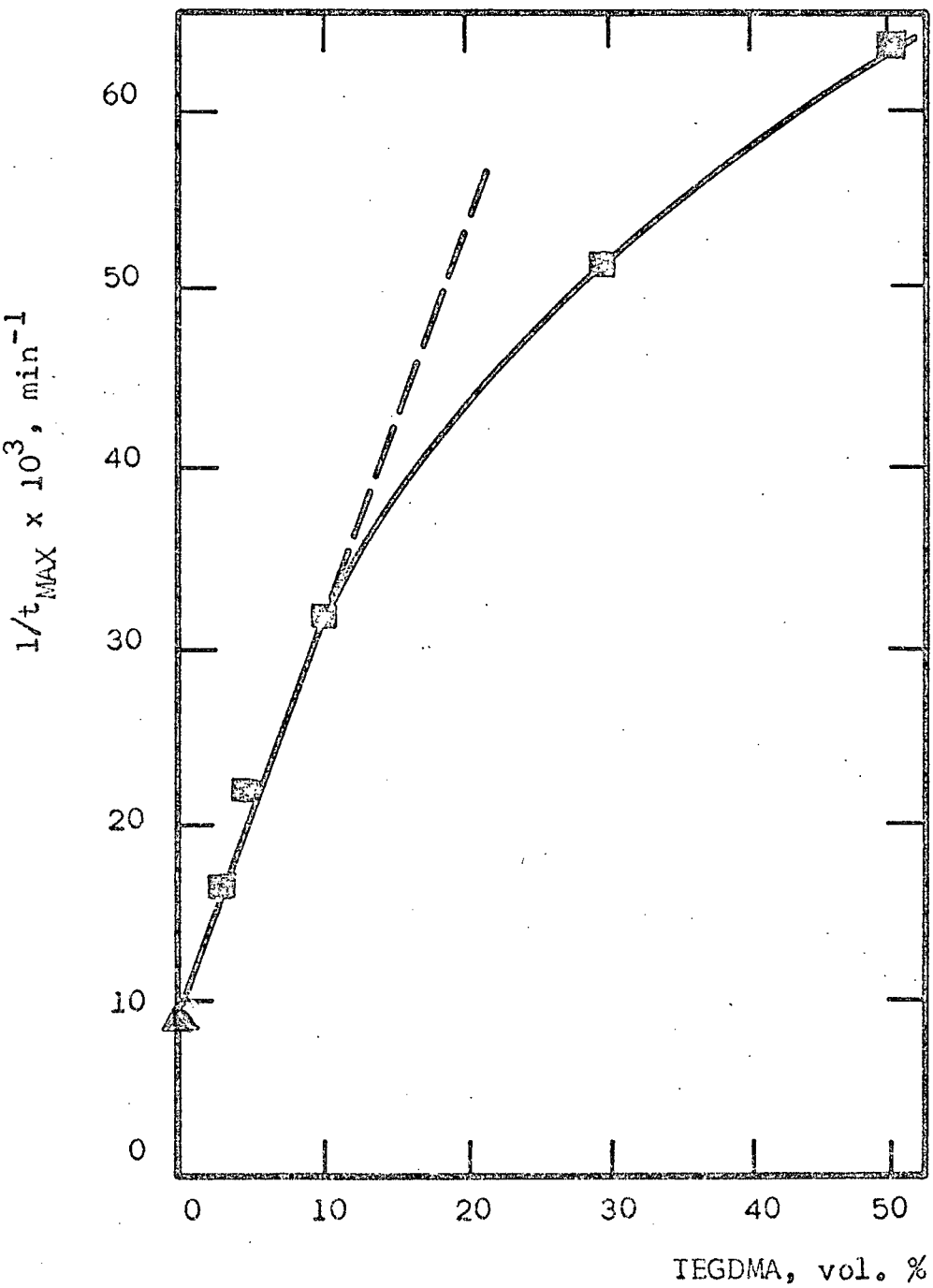


Figure 4-4. Relationship between t_{MAX} and divinyl monomer (DVM) volume concentration in MMA-DVM comonomer mixtures.

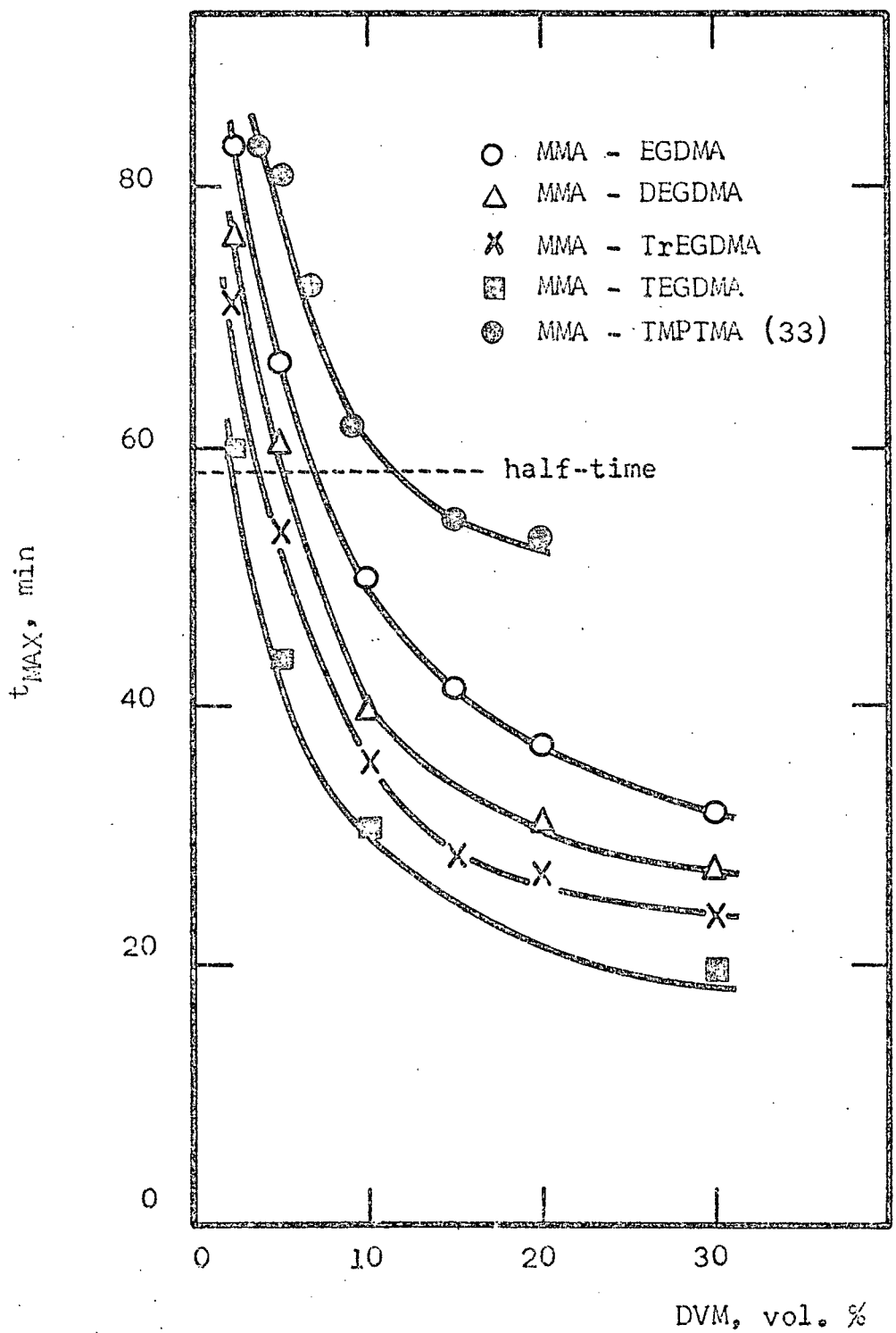


Figure 4-5. Relationship between t_{GEP} and divinyl monomer (DVM) volume concentration in MMA-DVM comonomer mixtures.

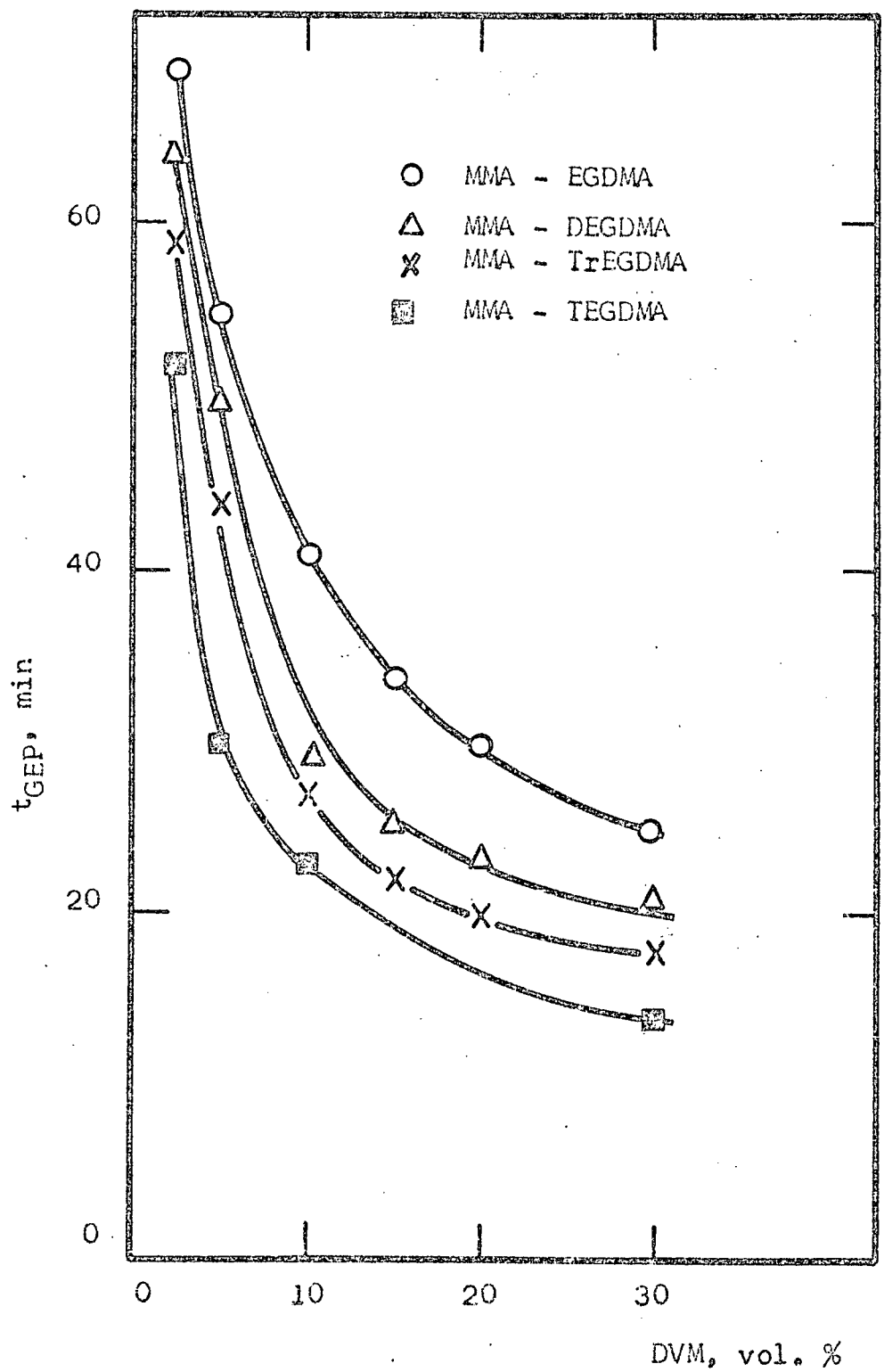


Figure 4-6. Polymerization rate coefficients in "Activation" (PRC_I) and "Acceleration" (PRC_{II}) periods as functions of divinyl monomer (DVM) volume concentration in MMA-DVM comonomer mixtures.

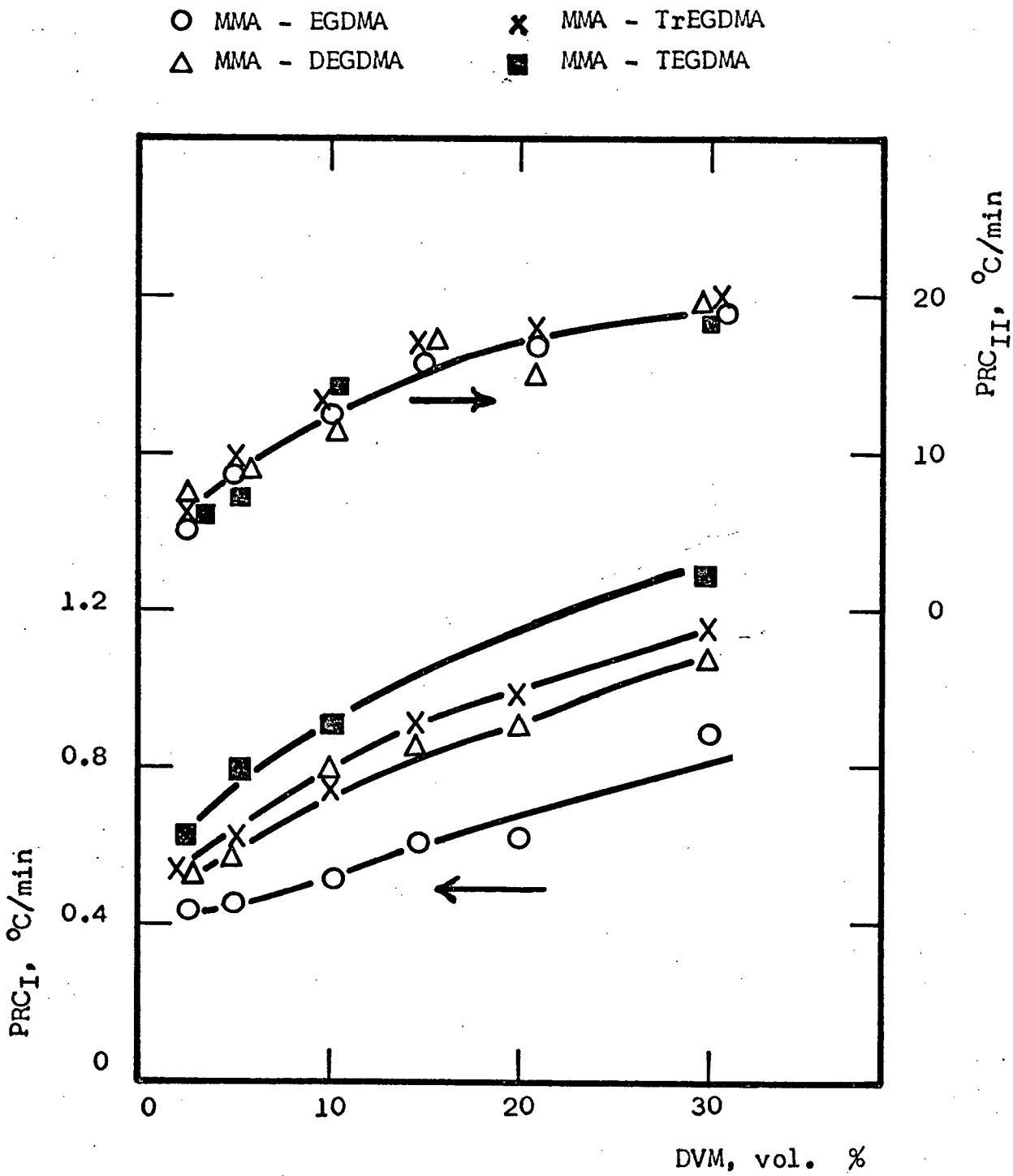


Figure 4-7. Relationship between t_{MAX} and t_{GEP} for different MMA-DVM comonomer systems and the S- TEGDMA system.

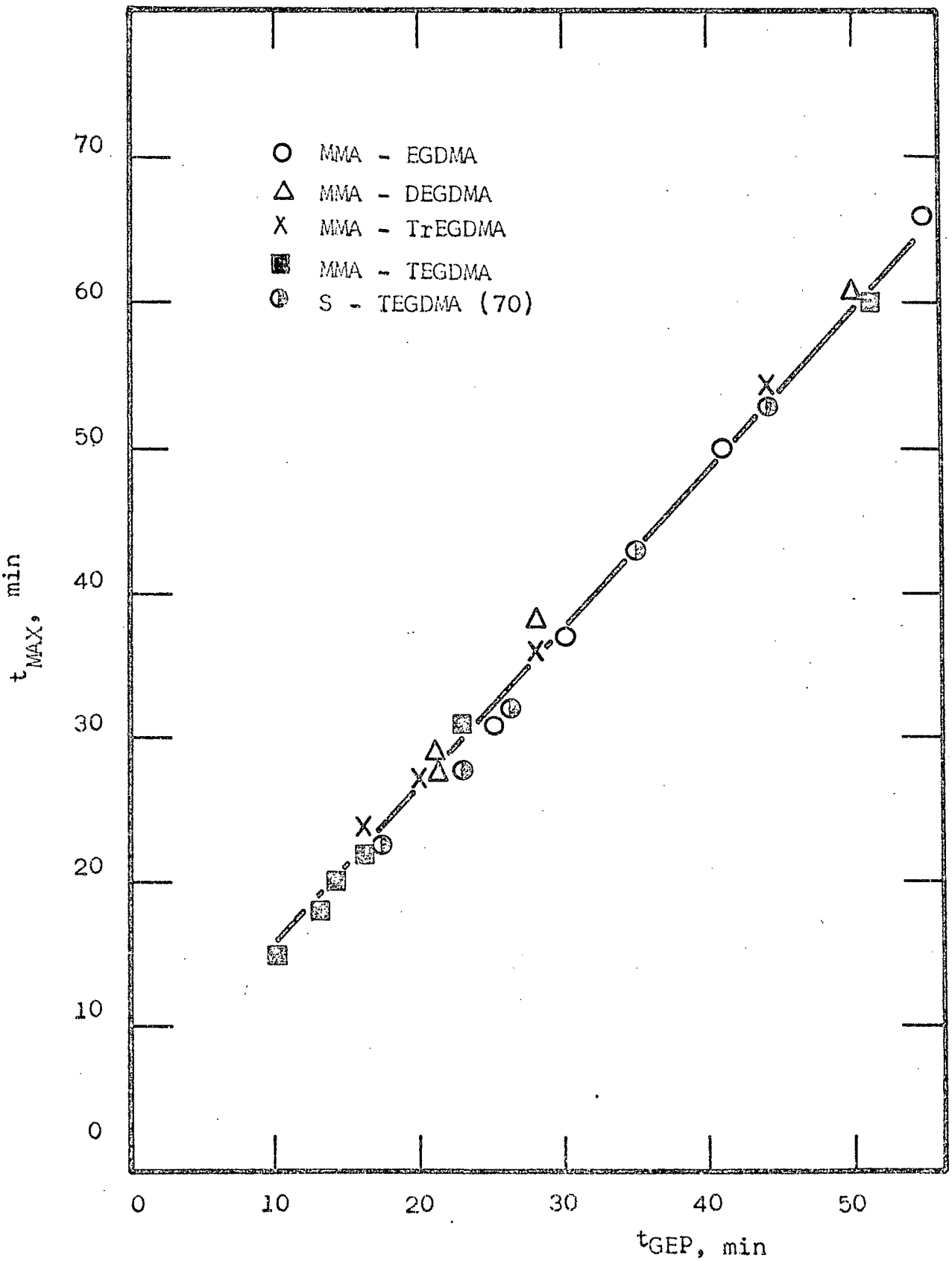


Figure 4-8. Relationship between overall curing rate ($1/t_{MAX}$) and DVM concentration in MMA-DVM mixtures.

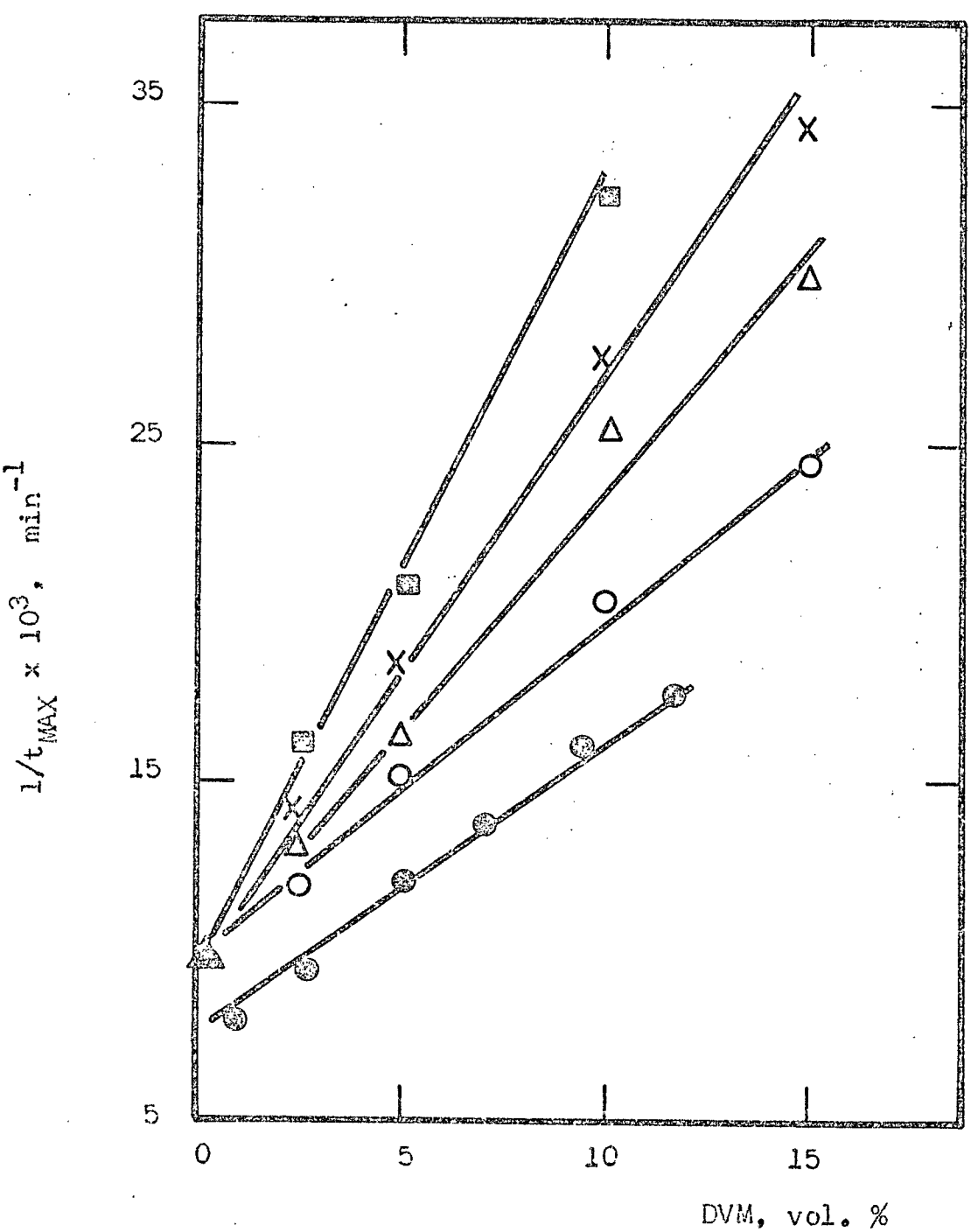


Figure 4-9. Overall acceleration constant (K) and its reciprocal (1/K) as functions of divinyl monomer connection number (CN_{DVM}, Table 3-1).

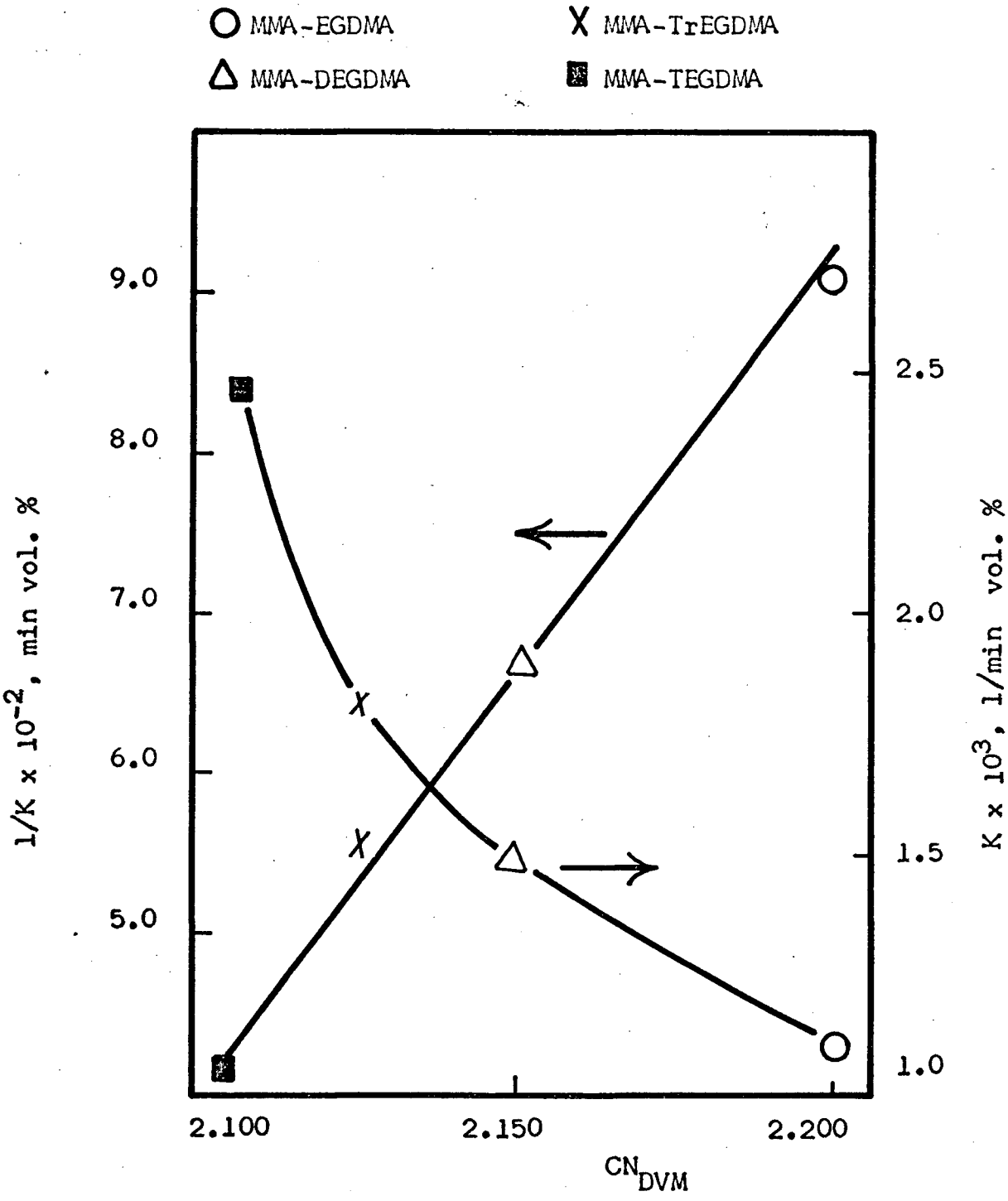


Figure 4-10. Relationship between overall curing rate ($1/t_{MAX}$) and DVM concentration in t-butyl styrene (TBS)-DVM mixtures. Evaluation of original heat-catalyst data from (53).

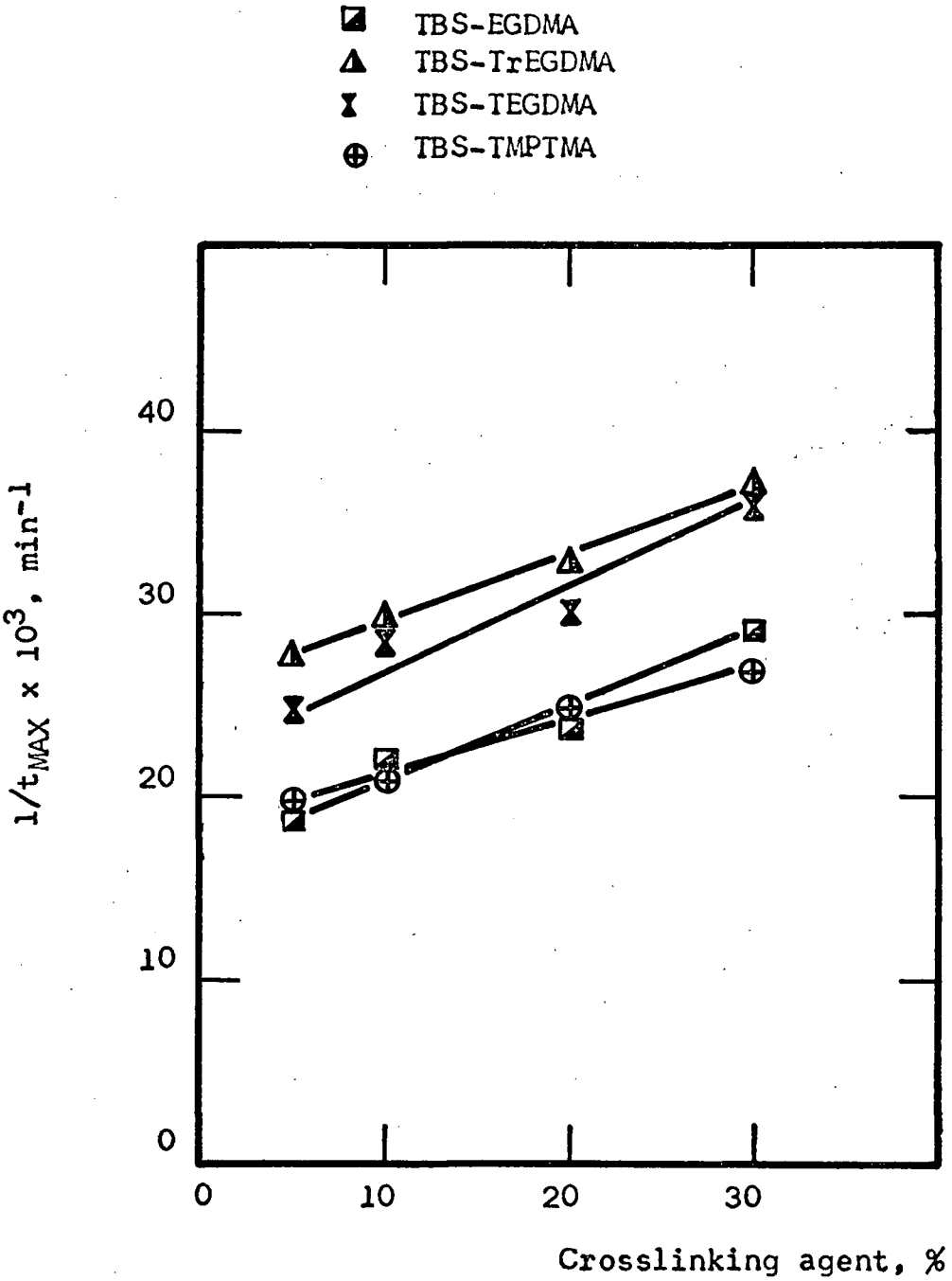


Figure 4-11. Overall curing rate ($1/t_{MAX}$) of TEGDMA as a function of radiation dose rate.

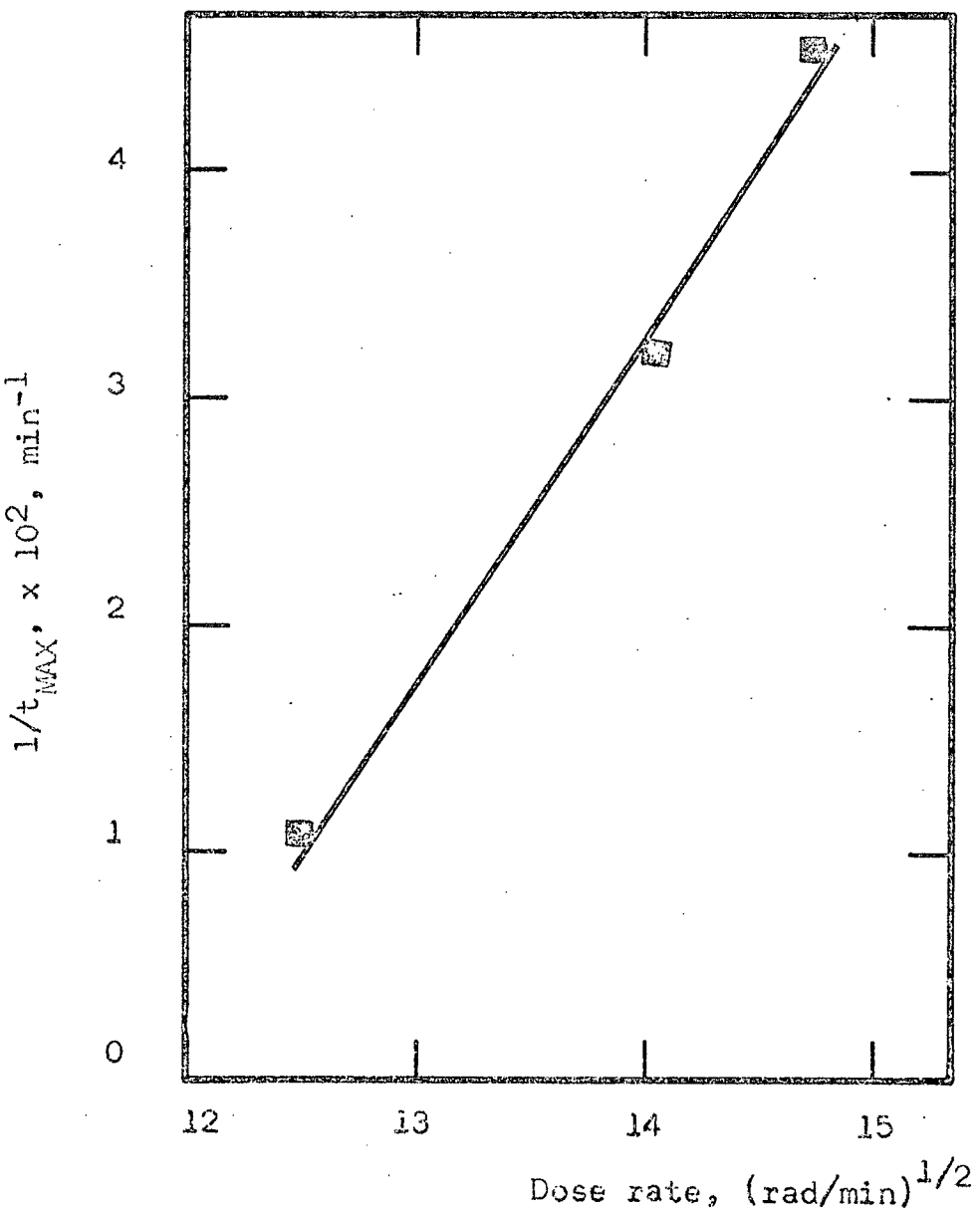


Figure 4-12. Shape of thermomechanical curves for MMA-EGDMA polymer products. Numbers indicate per cent of EGDMA in comonomer mixture and copolymer connection number (CN_{co}).

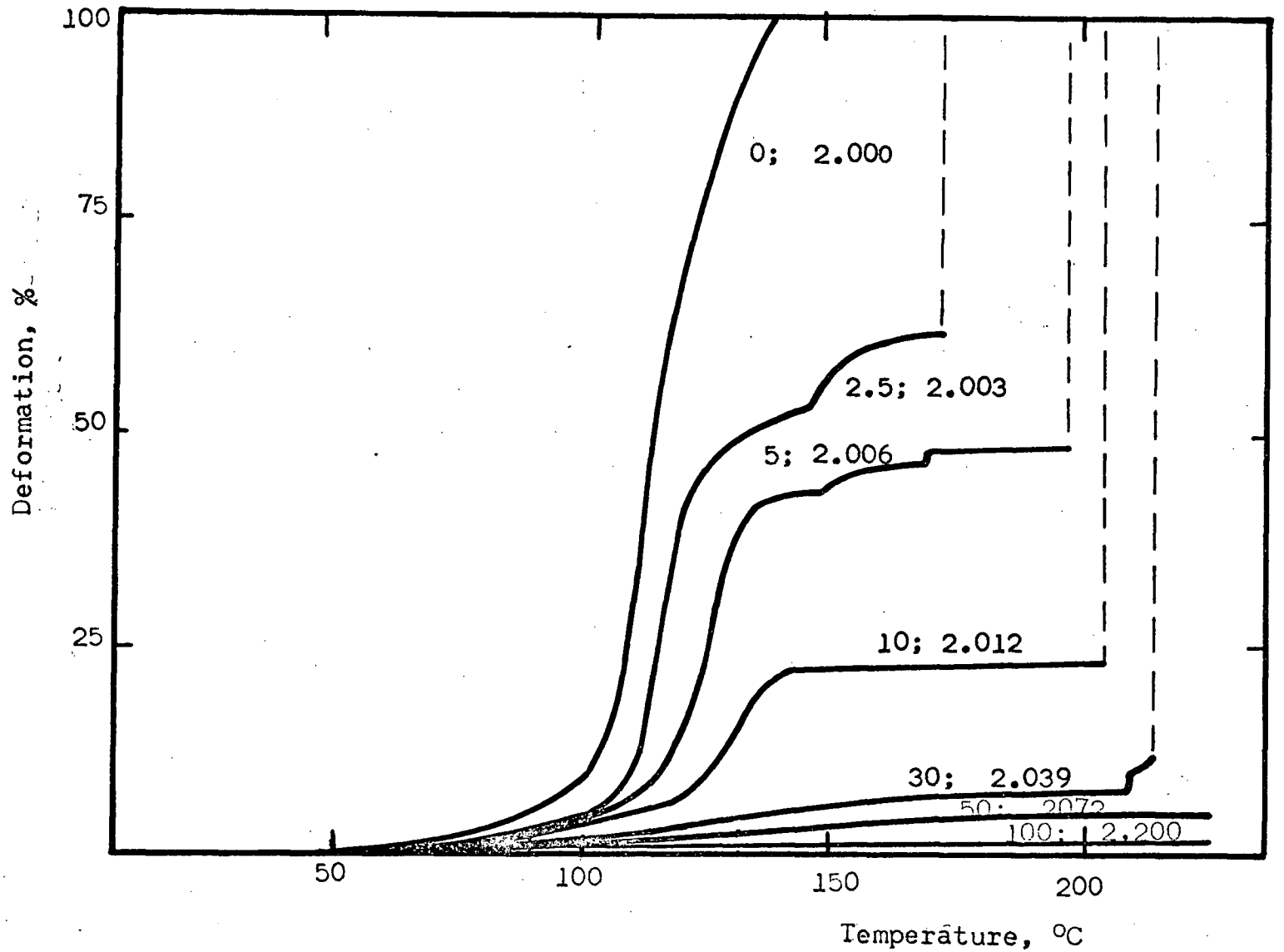


Figure 4-13. Shape of thermomechanical curves for MMA-TEGDMA polymer products. Numbers indicate per cent of TEGDMA in comonomer mixture and copolymer connection number (CN_{co})

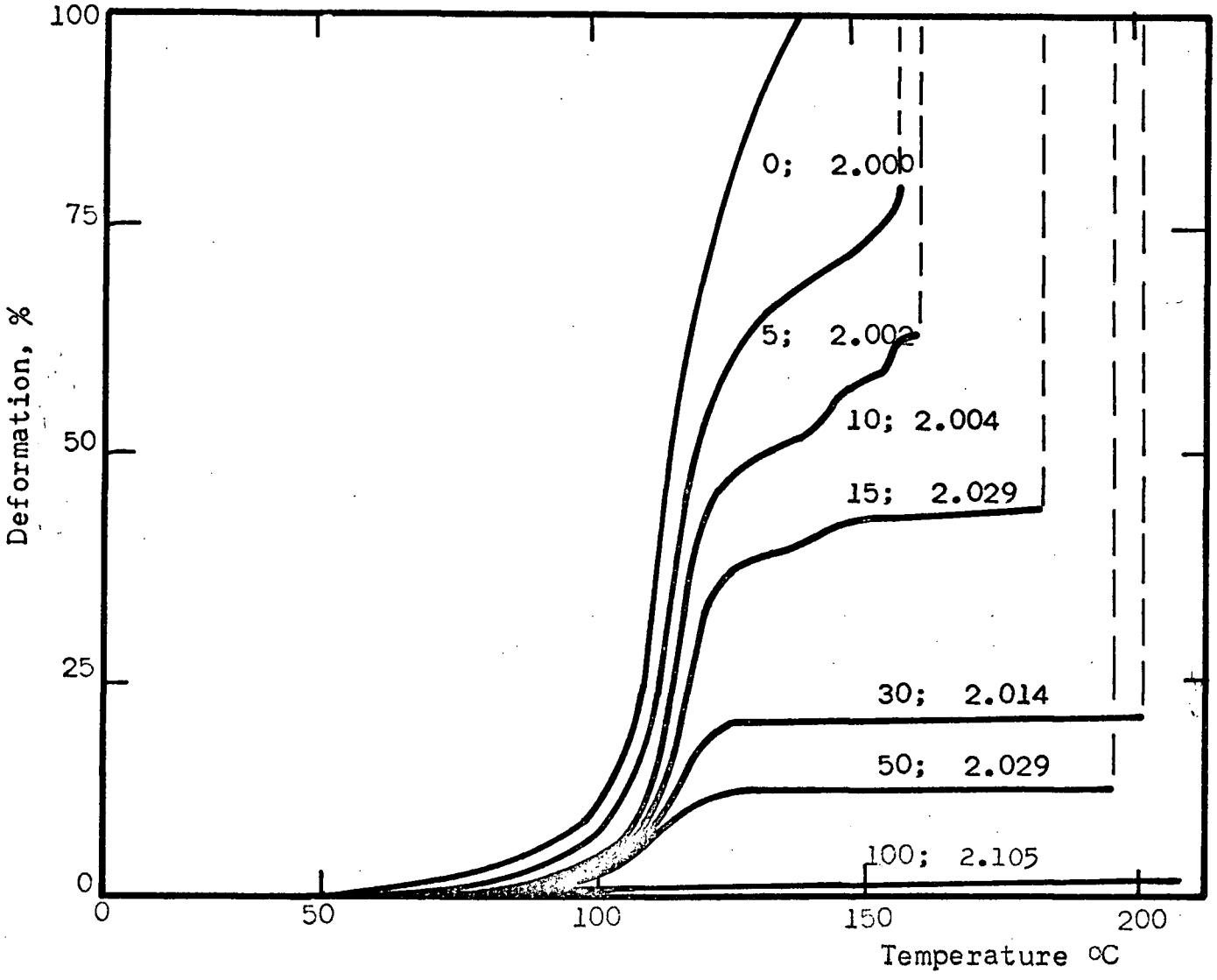


Figure 4-14. Glass transition temperature (T_g) as a function of copolymer connection number (CN_{co}) for different MMA-DVM polymer products.

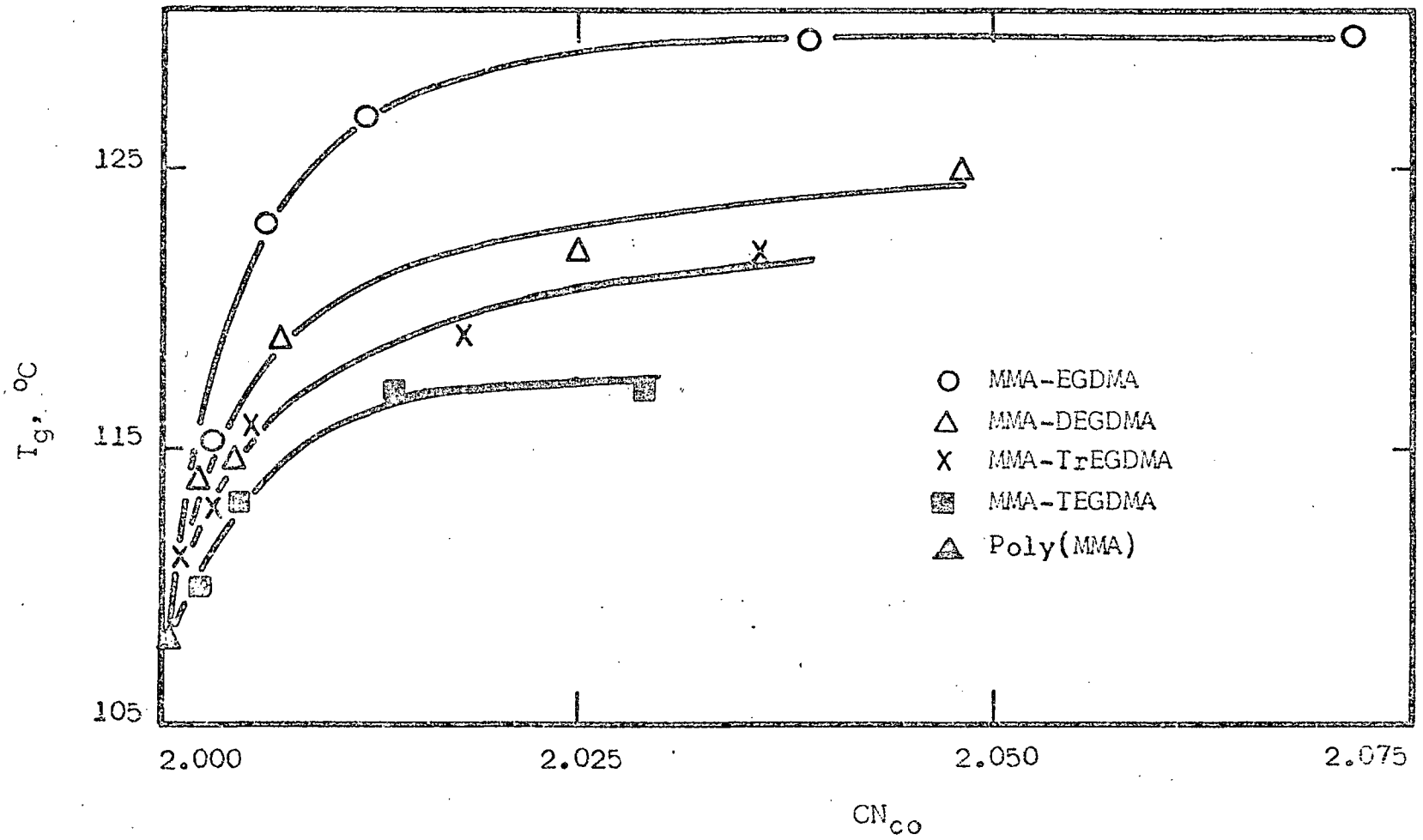


Figure 4-15. Thermal deformation degree (TDD) and thermal distortion temperature (TDT) as functions of copolymer connection number (CN_{co}) for different MMA-DVM polymer products.

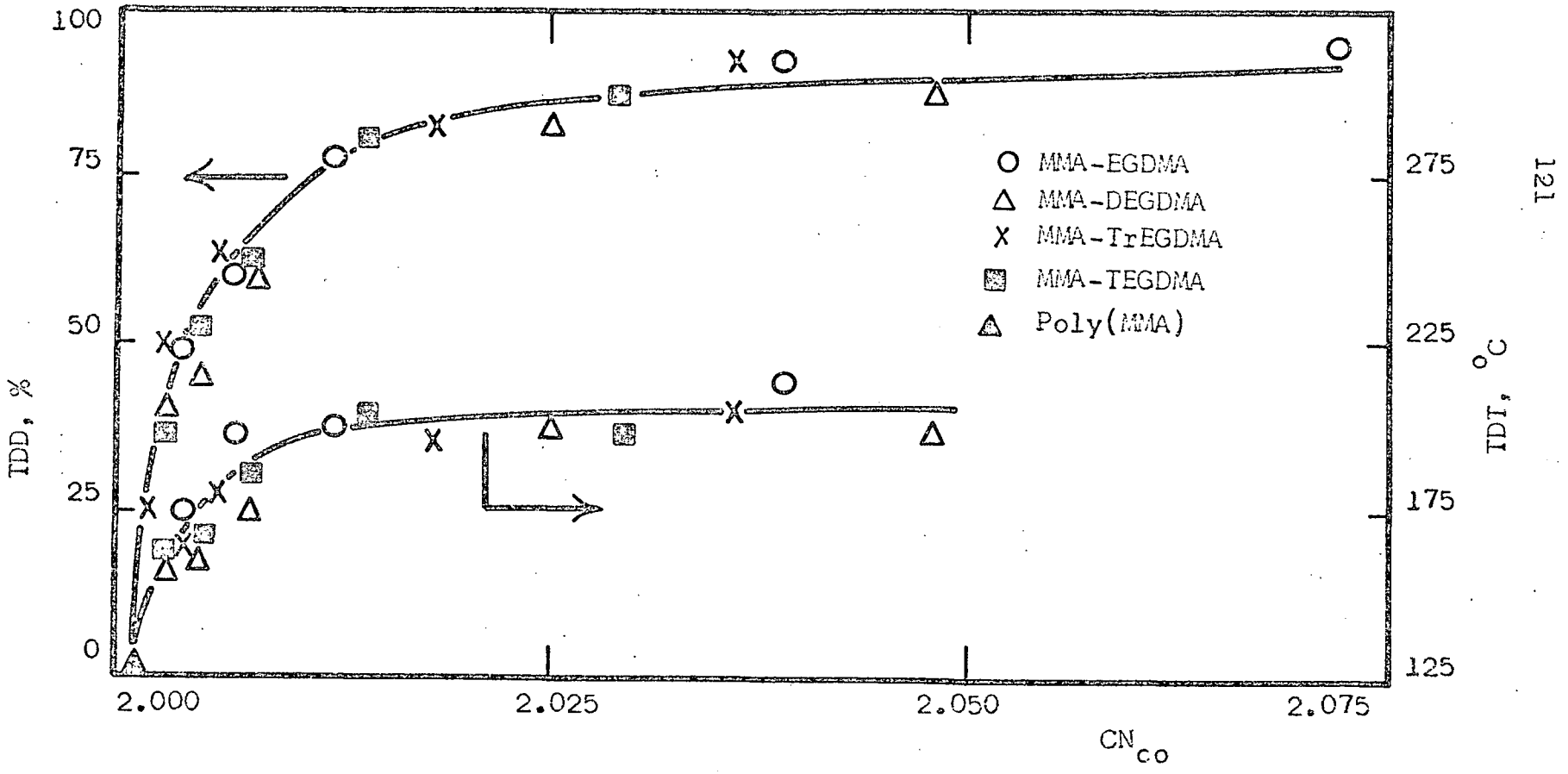


Figure 4-16. Linear thermomechanical deformation coefficient (LTDC) as a function of divinyl monomer (DVM) concentration in MMA-DVM polymer products.

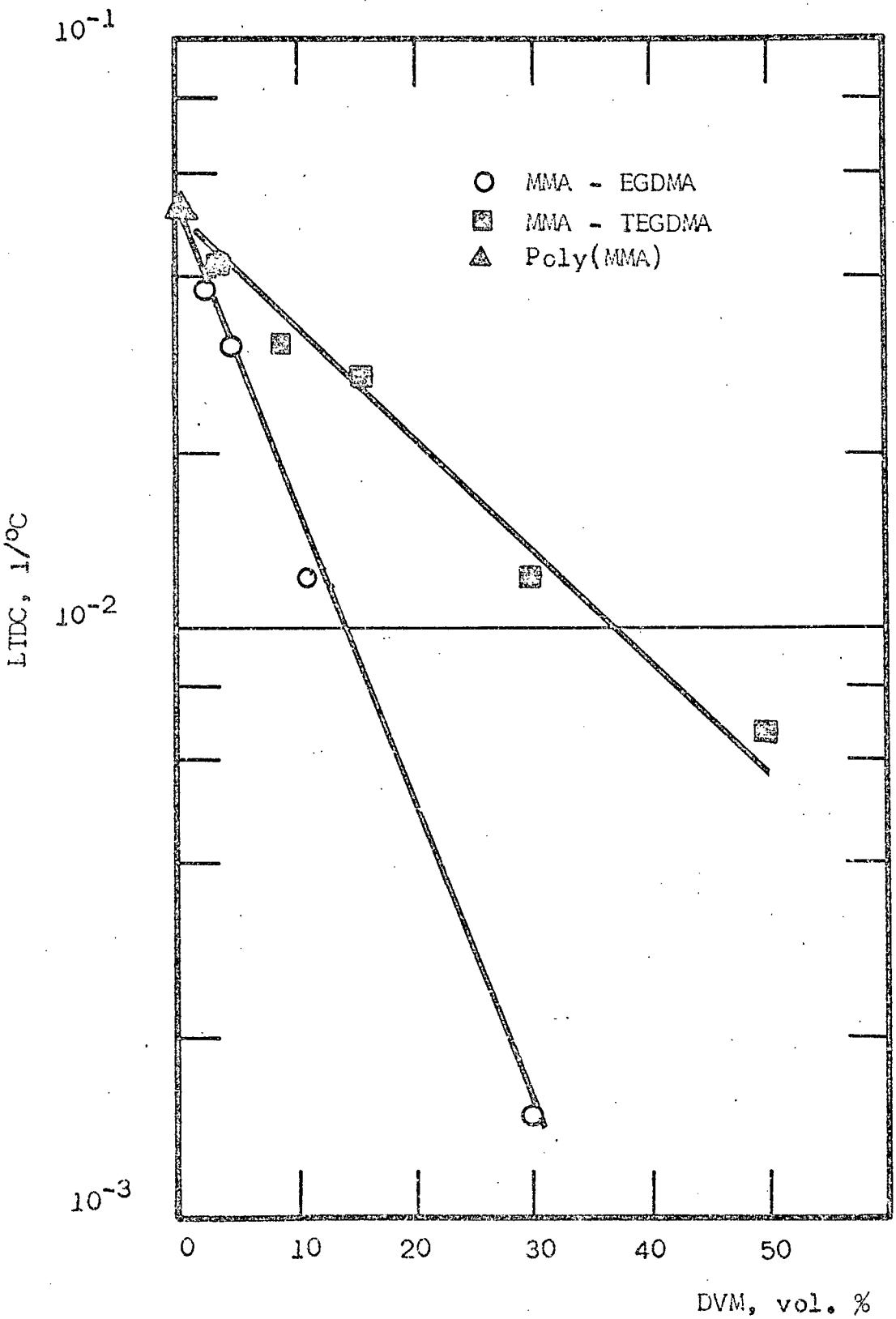


Figure 4-17. Linear thermomechanical deformation coefficient (LTDC) as a function of copolymer connection number (CN_{co}) for different MMA-DVM polymer products.

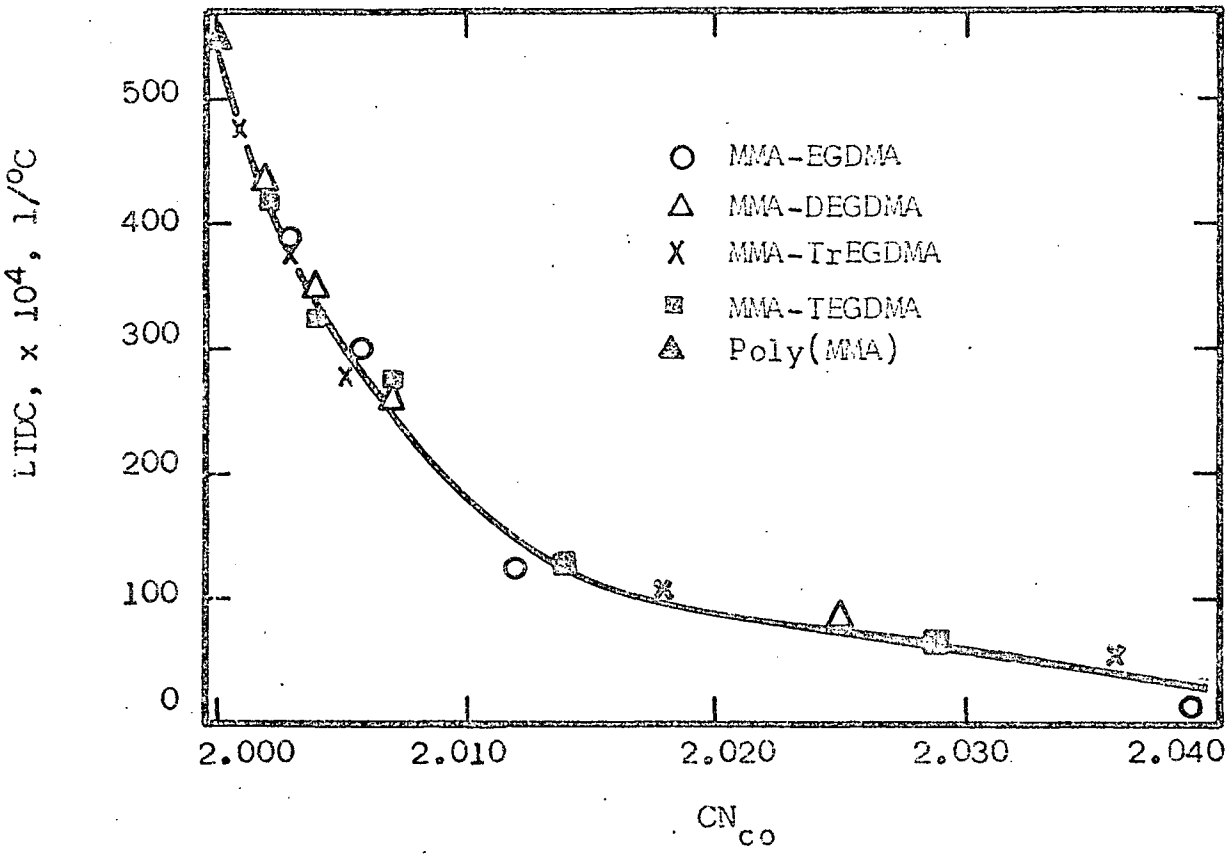


Figure 4-18. Shape of compression stress-strain curves for MMA-EGDMA polymer products. Rate of strain 0.1 cm/min.

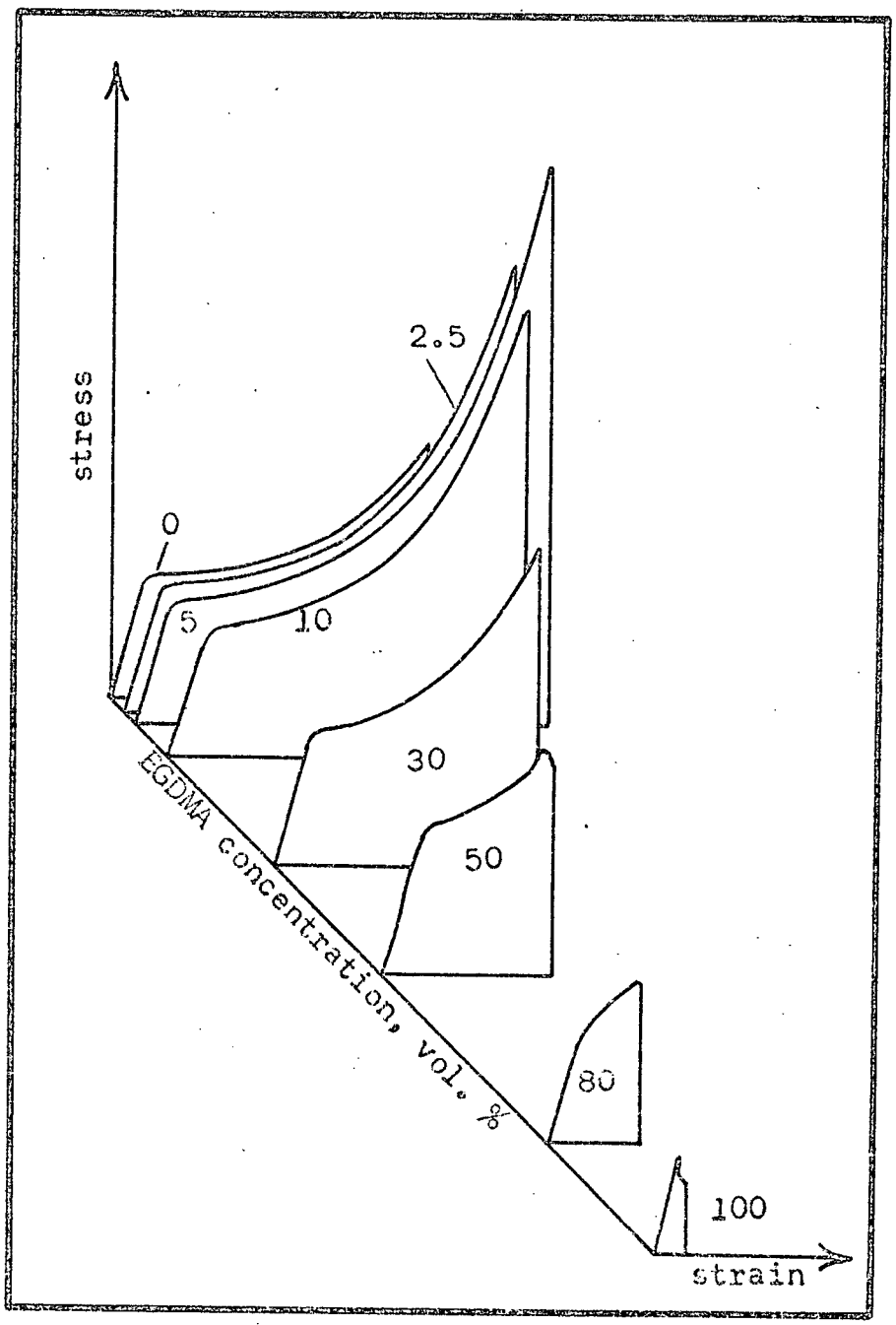


Figure 4-19. Shape of compression stress-strain curves for MMA-TEGDMA polymer products. Rate of strain 0.1 cm/min.

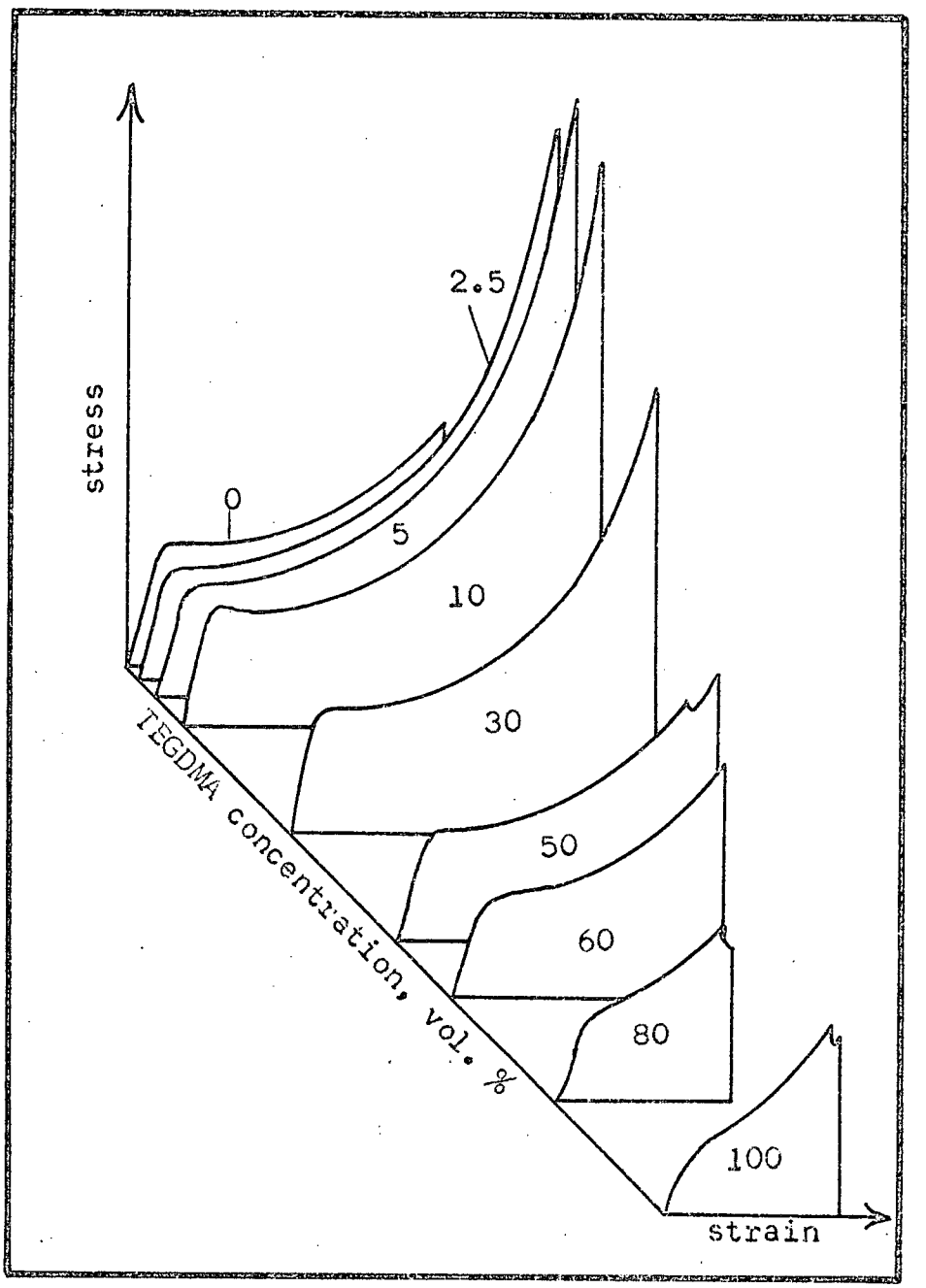


Figure 4-20. Compression stress-strain parameters as functions of comonomer composition. The MMA-EGDMA comonomer system. (Rate of strain 0.1 cm/min.)

⊖ Compression stress at rupture, $kg/cm^2 \times 10^{-2}$

✱ Compression strain at rupture, %

Δ Area under stress-strain curve, F, cm^2.

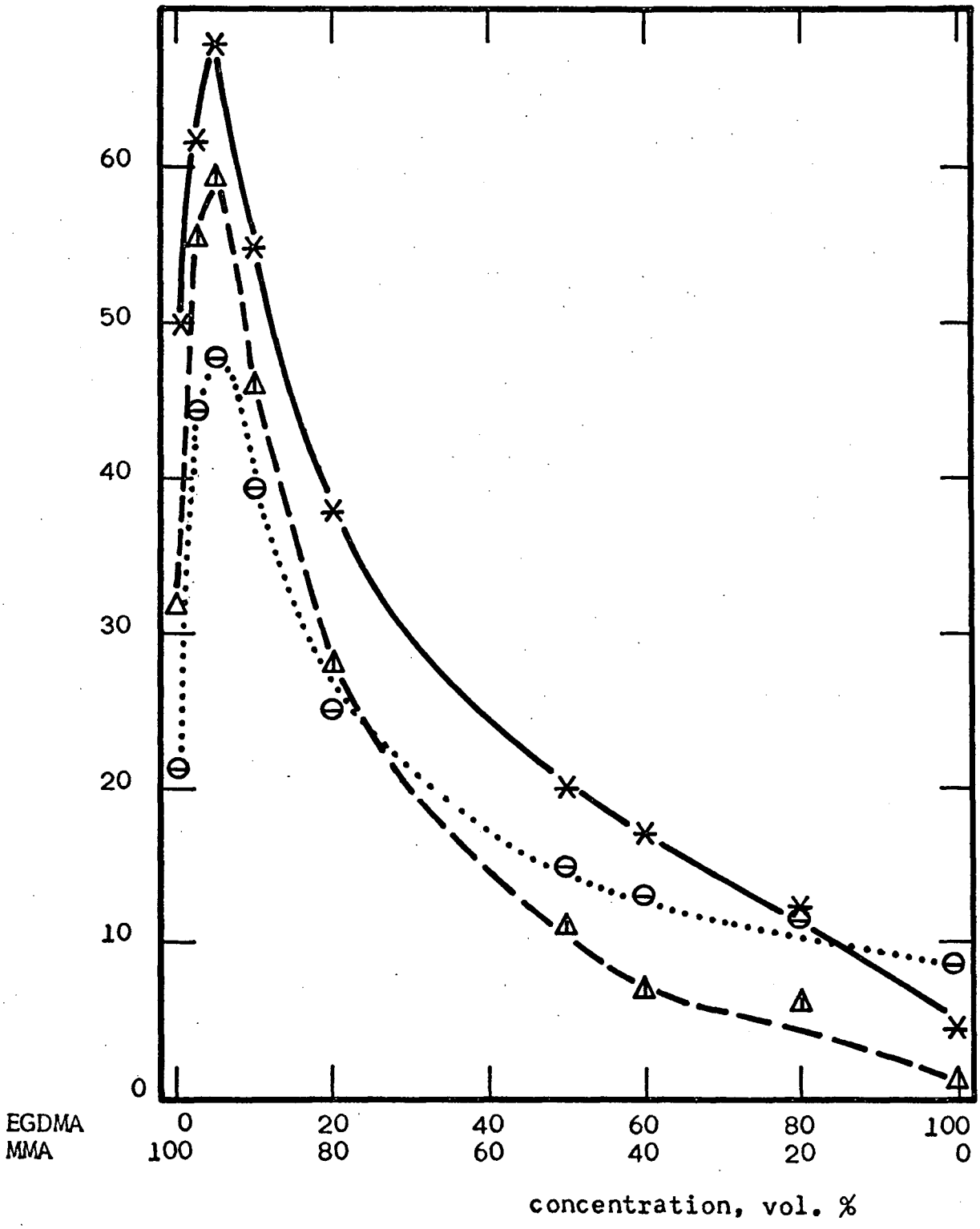


Figure 4-21. Compression stress-strain parameters as functions of comonomer composition. The MMA-DEGDMA comonomer system. (Rate of strain 0.1 cm/min.)

⊖ Compression stress at rupture, $kg/cm^2 \times 10^{-2}$
✳ Compression strain at rupture, %
△ Area under the stress-strain curve F, cm^2.

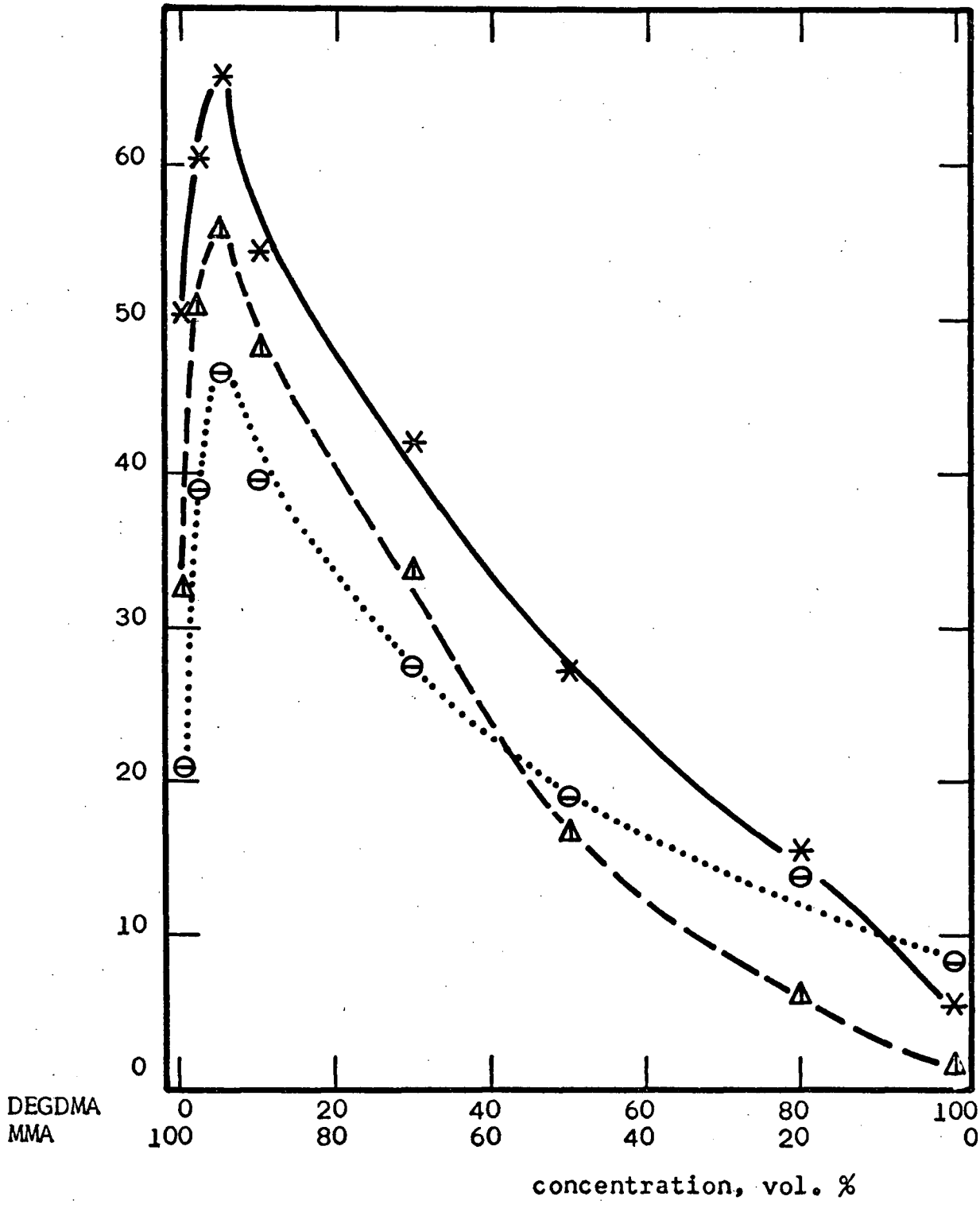


Figure 4-22. Compression stress-strain parameters as functions of comonomer composition. The MMA-TrEGDMA comonomer system. (Rate of strain 0.1 cm/min).
⊖ Compression stress at rupture, $kg/cm^2 x 10^{-2}$
✳ Compression strain at rupture, %
△ Area under the stress-strain curve F, cm^2

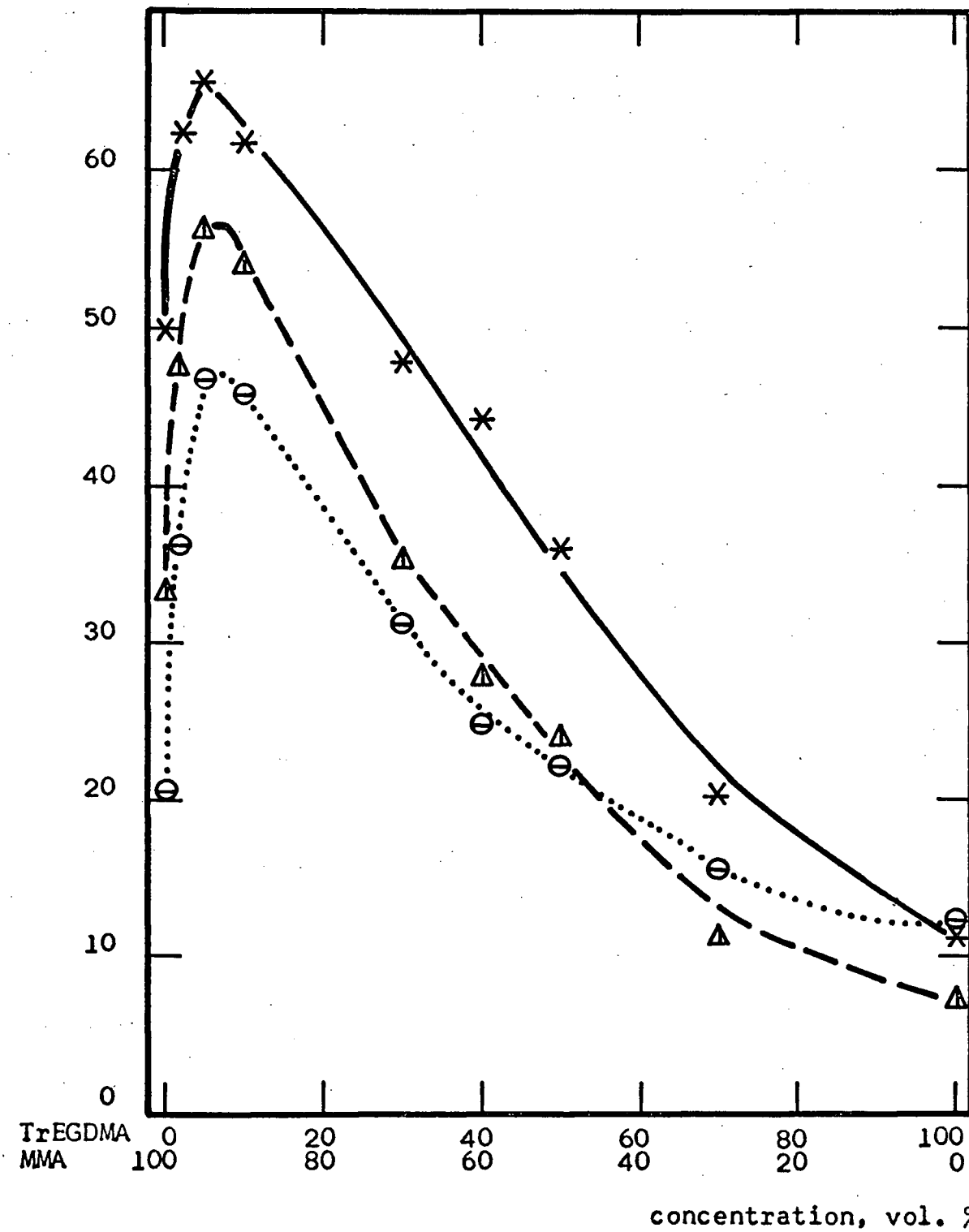


Figure 4-23. Compression stress-strain parameters as functions of comonomer composition. The MMA-TEGDMA comonomer system. (Rate of strain 0.1 cm/min.)
⊖ Compression stress at rupture, $kg/cm^2 \times 10^{-2}$
✱ Compression strain at rupture, %
△ Area under the stress-strain curve F, cm^2

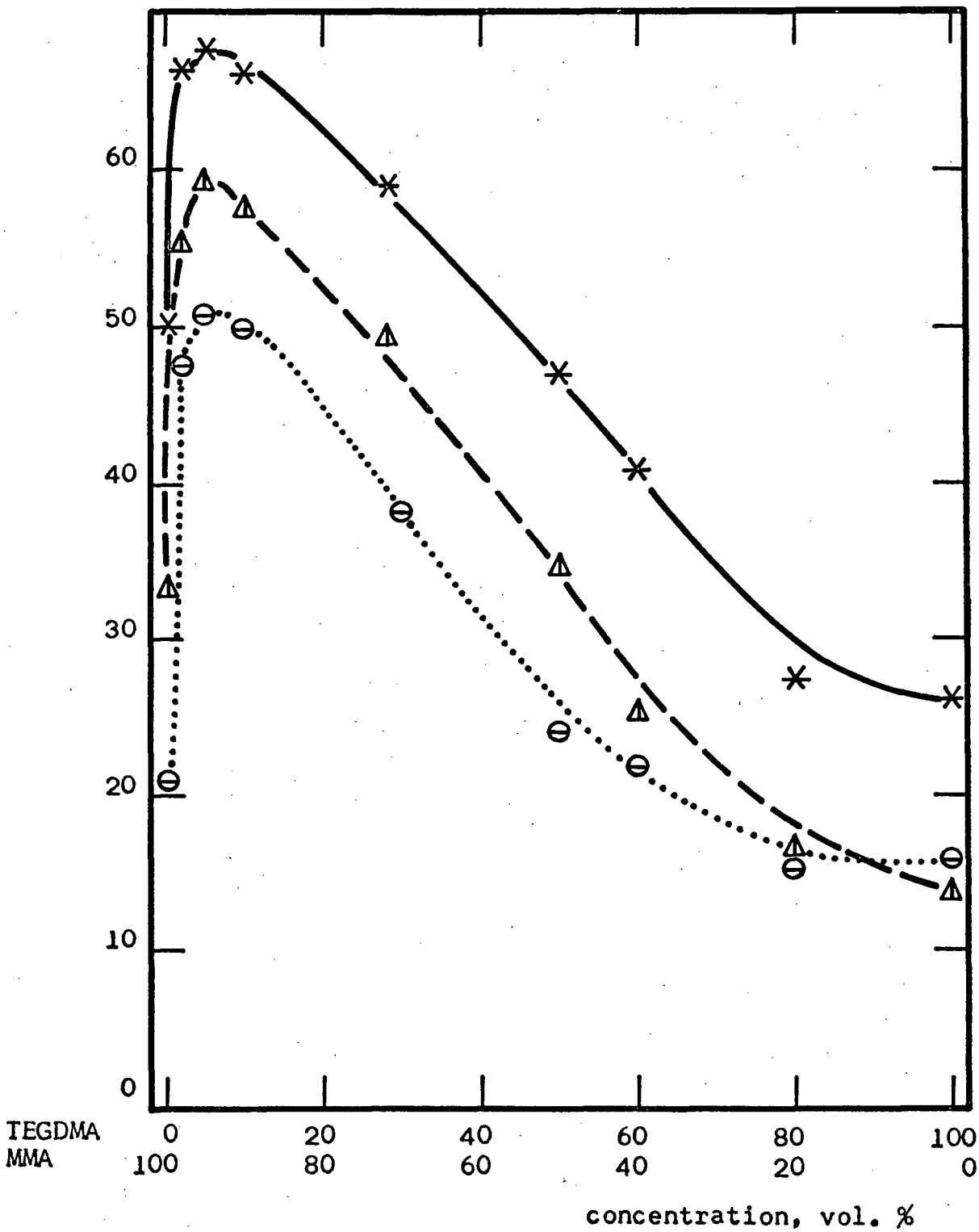


Figure 4-24. Compression stress at rupture as a function of copolymer connection number (CN_{co}) for different MMA-DVM polymer products.

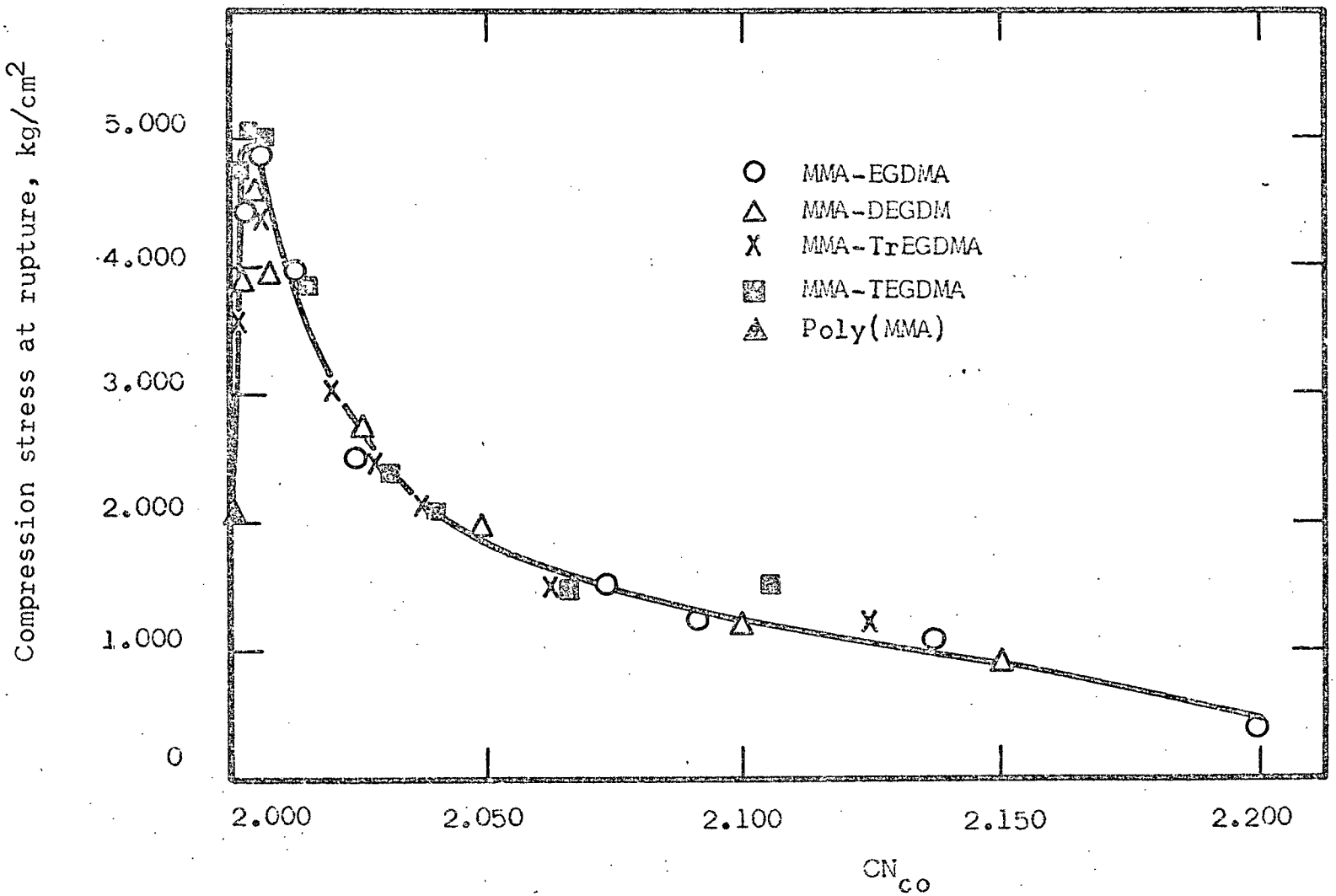


Figure 4-25. Relationship between area under the compression stress-strain curve (F) and plastic deformation for different MMA-DVM polymer products.