Radiation-Induced Solid-State Polymerization in Binary Systems. VI. Polymerization of Vinyl Compounds in the Supercooled Liquid Phase

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SUMMARY

The radiation-induced polymerization of glass-forming systems containing vinyl monomers was investigated. Irradiation below the second-order transition temperature (T_g) of the systems causes no in-source polymerization but does cause a very rapid postpolymerization in the course of heating above T_g. Differential thermal analysis was carried out to estimate T_g and to follow the postpolymerization.

In both in-source polymerization and postpolymerization, temperature dependence of the rate of polymerization shows a maximum value just above T_g. When the systems are crystallized, the rate and degree of polymerization are reduced.

INTRODUCTION

In previous papers [1, 2] it was shown that many systems containing acrylic monomers formed glassy phases based on the mutual molecular interaction of the components.

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Rapid in-source polymerizations could take place only in the temperature range above the glass transition temperature (T_g), and the rate of these polymerizations had a maximum value near the T_g of these systems.

Further investigation has been made in order to clarify the characteristics of so-called glassy state polymerization. The glassy systems can be classified into the following two types:

One type is the system in which the monomer itself interacts with matrix solvent to form a glassy phase. The authors have studied mainly this type of glassy system in previous papers [1, 2], for example, the systems consisting of acid-amide combination, in which one component is acrylamide or acrylic acid.

The other type is the system in which the monomer is dissolved into a nonpolymerizable glassy matrix. The present paper reports polymerization in this second type of system.

It has been reported that in the case of vinyl acetate polymerization actually proceeded in the glassy state solely during irradiation [3]. However, Nakatsuka et al. [4] reported that vinyl acetate did not essentially polymerize during irradiation in the glassy state, but really polymerized at a temperature just above T_g, i.e., in the supercooled liquid state. We obtained the same results in the present study as Nakatsuka et al.

EXPERIMENTAL

Materials

The materials were purified by the usual method: Methyl methacrylate (MMA) was distilled, bp, 43°C at 90 mm Hg, n_D^{25} = 1.412; propionic acid (PA), bp, 74°C at 60 mm Hg, n_D^{25} = 1.387; acrylonitrile (AN), bp, 47°C at 500 mm Hg, n_D^{25} = 1.389; and styrene (ST), bp, 50°C at 24 mm Hg, n_D^{25} = 1.544. The gas chromatographic analysis showed no impurities in these monomers. Acetamide (AcM) was recrystallized from dry benzene solution and dried under reduced pressure, mp, 82.1°C. Succinic acid (SA) was recrystallized from methanol solution, mp, 185°C.

Thermal Measurement

A differential thermal analyzer (AGNE Research Center Company, Ltd.) was used for estimating T_g of the systems and for following the post-polymerizations. In the sample holder, made of beryllia, 25 mm in diam

by 30 mm long, two wells were placed for the cell. The chromel-alumel thermocouple was placed in the center of the differential thermal analysis (DTA) cell. The cell was made of glass, 8 mm in diam by 18 mm high; at the center was a small well, 2.3 mm in diam by 7 mm deep, for the thermocouple.

NMR Measurement

A broad-line NMR (Varian V-4210A rf unit) (14 MHz) was used.

Procedures

Each sample was degassed three times in glass ampoules (about 1 ml) and in the DTA cells (about 0.1 ml) and was sealed off in vacuum. The samples were irradiated by γ-rays from a ^{60}Co (90,000 Ci) source at the desired temperature in the case of in-source polymerization, and at liquid nitrogen temperature (-196°C) in the case of postpolymerization.

In all cases, the samples kept the transparent appearance of the glassy phase at -196°C, though many cracks were observed.

For the DTA measurement, the cells and the cell holder were maintained carefully at -196°C and then heated at a controlled rate. The heating rate is expressed in units of mV/min. One mV/min corresponds to 40°C/min near -196°C, 32°C/min near -100°C, and 25°C/min above 0°C.

Pure alumina was used as the reference material. The temperature calibration of the instrument was achieved by the equilibrium (solid-gas) temperature of CO_2 and the melting of mercury. The DTA was found to be precise to ±0.5°C and an accuracy of ±1.0°C.

For the NMR measurement, the sample (about 1 ml) was sealed in a glass ampoule (1 cm in diam by 20 cm long) and measured at desired temperatures.

For the postpolymerization, the sample was irradiated at -196°C, immersed in a Dewer vessel controlled at the desired temperature, and kept for 1 hr to perform the postpolymerization reaction.

Cryostats were used to obtain the following temperatures for the postpolymerization: melting point (mp) of methanol, - 97°C; mp of solid CO_2-acetone mixture, -78°C; mp of solid CO_2-methanol mixture, -70°C; mp of chloroform, -63.5°C; mp of methyl methacrylate, -48°C; mp of benzyl chloride, -39°C; mp of ice-methanol mixture, -30°C. Temperatures of -20°C were obtained by the use of a thermostat.
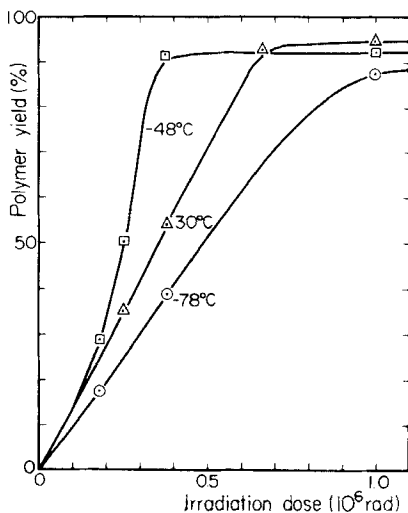
Fig. 1. In-source polymerization of methyl methacrylate in propionic acid-acetamide system. Polymerization temperatures, °C: Δ, +30; □, -48; O, -78. Dose rate: 6.2 × 10⁴ rad/hr in vacuo. Composition, mole %: MMA, 13; PA, 38; AcM, 49.

The polymer obtained was precipitated in cooled methanol of the same temperature as that of polymerization, and polymer yield was determined gravimetrically.

MMA, AN, and ST could not form a glassy state by themselves with the same treatment as the sample; that is, they have no thermal anomaly on the DTA traces heated from -170°C to their melting points (-48, -85, and -30°C, respectively). However, postpolymerizations of the bulk MMA, AN, and ST were not observed in DTA traces.

The molecular weight of PMMA was determined by viscometry at 25°C in benzene using the following equation [5]:

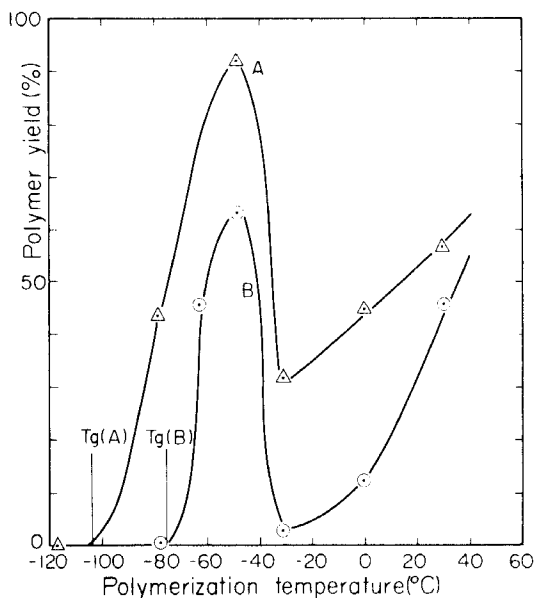$$[\eta] = 0.74 \times 10^{-4} \times M^{0.76}$$

Fig. 2. Polymer yield as a function of polymerization temperature. Dose rate: 6.2 × 10⁴ rad/hr. A. △: Methyl methacrylate in propionic acid-acetamide system. Composition, mole %: MMA, 13; PA, 38; AcM, 49. Polymerization time: 6.0 hr in vacuo. B. ○: Methyl methacrylate in succinic acid-acetamide system. Composition, mole %: MMA, 10; SA, 18; AcM, 72. Polymerization time: 3.9 hr in vacuo.

RESULTS AND DISCUSSION

In-Source Polymerization

The behavior of in-source polymerization at various temperatures is shown in Fig. 1. The influence of the nature of the glass-forming matrix on the polymerization rate of MMA is indicated in Fig. 2, and of AN in Fig. 3. T_g values of the systems were determined by DTA as shown in Figs. 4 and 5.

Figure 4 shows the DTA traces of the PA-AcM and MMA-PA-AcM systems. The PA-AcM system T_g is -92°C and its crystallization temperature (T_c) is -42°C. On the other hand, T_g decreased to -104°C with
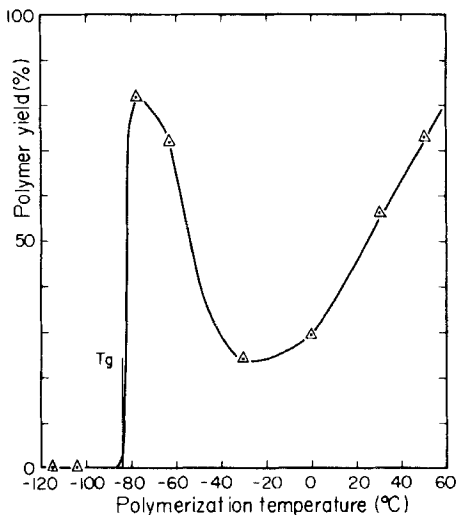
Fig. 3. Polymer yield as a function of polymerization temperature. Acrylon-
itrile in succinic acid-acetamide system. Composition, mole %: AN, 15;
SA, 17; AcM, 68. Polymerization time: 4.8 hr in vacuo. Dose rate: 1.67 X
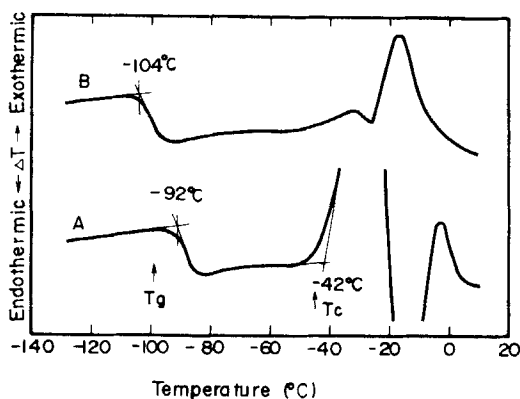10^4 rad/hr.

Fig. 4. DTA traces of acid-amide system indicating glass transition tempera-
tures. A. Propionic acid (45 mole %)-acetamide (55 mole %) system.
B. Methyl methacrylate (13 mole %)-propionic acid (38 mole %)-acetamide
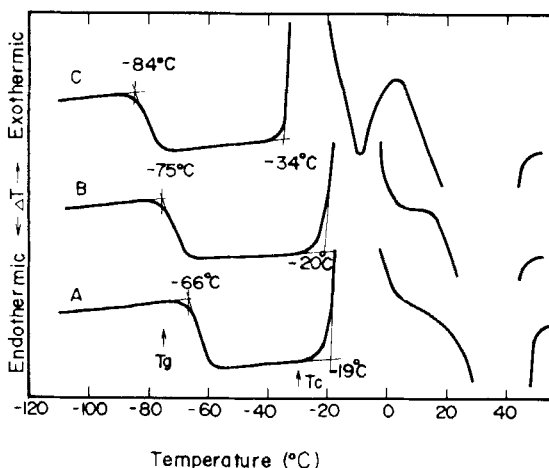(49 mole %) system. Heating rate: 0.2 mV/min.

Fig. 5. DTA traces of acid-amide system indicating glass transition tempera-
tures. A. Succinic acid (20 mole %)-acetamide (80 mole %) system.
B. Methyl methacrylate (10 mole %)-succinic acid (18 mole %)-acetamide
(72 mole %) system. C. Acrylonitrile (15 mole %)-succinic acid (17 mole %)-
acetamide (68 mole %) system. Heating rate: 0.2 mV/min.

the addition of MMA, and a clear T_C was not observed in this system. Fig-
ure 5 shows the DTA traces of the SA-AcM (T_g, -66°C; T_C, -19°C), MMA-
SA-AcM (T_g, -75°C; T_C, -20°C), and AN-SA-AcM (T_g, -84°C; T_C, -34°C)
systems.

It is obvious that in these systems polymerization does not occur below
T_g, owing to the inhibition of monomer diffusion, but proceeds very
rapidly in the temperature range just above T_g, where the rate of poly-
merization has an apparent maximum value due to the rapid change in
viscosity of the system. In the temperature range above T_g, polymeri-
zation reaction starts to grow; however, near T_g, diffusions of both the
growing polymer chain and the monomer are restricted in these systems.
With increases in temperature, the restriction on the propagation reaction
is loosened, but not on the termination reaction. This phenomenon re-
sults in the acceleration of the polymerization rate. Then the polymeri-
zation reaction reaches the usual stationary state in the liquid phase.

The molecular weights of polymers shown in Fig. 2A are shown in
Table 1. The molecular weights of polymers obtained by the poly-
merization of MMA in the supercooled liquid phase are higher than those
obtained in the usual liquid phase.

Table 1. Molecular Weights of Polymers Obtained in the In-Source Polymerization of the Methyl Methacrylate-Propionic Acid-Acetamide System[a]

Polymerization temperature, °C	$[\eta]$	$Mn \times 10^{-6}$
-78 (in air)	2.80	1.03
-78 (in vacuo)	3.23	1.28
-48 (in vacuo)	3.50	1.42
-30 (in vacuo)	2.56	0.95
+30 (in vacuo)	2.16	0.75

[a]Composition, mole %: MMA, 13; PA, 38; AcM, 49. Irradiation: 6.2×10^4 rad/hr × 6 hr.
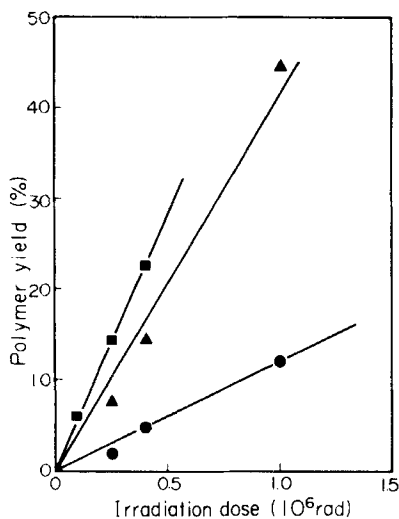

Fig. 6. In-source polymerization of styrene in propionic acid-acetamide system. Polymerization temperatures, °C: ▲, +30; ■, -48; ●, -78. Dose rate: 6.2×10^4 rad/hr in vacuo. Composition, mole %: ST, 13; PA, 39; AcM, 48.
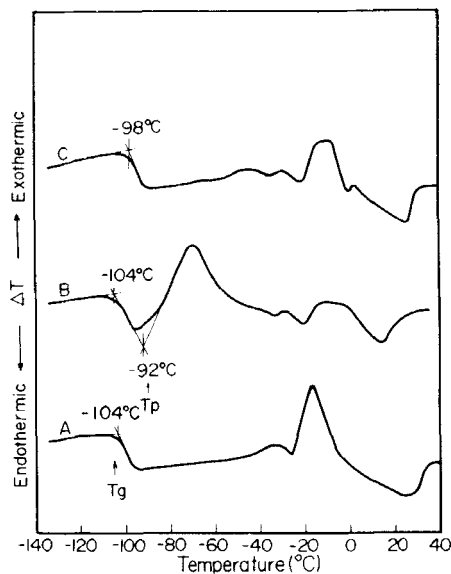
Fig. 7. DTA traces of methyl methacrylate-propionic acid-acetamide system. A. Before irradiation. B. Irradiated (4×10^5 rad/hr $\times$ 1 hr at $-196°C$). C. After B run. Heating rate: 0.2 mV/min.

Oxygen reduces the molecular weight of the polymer by attacking the propagating radical.

Figure 6 suggests that the polymerization behavior of the ST-PA-AcM system is quite similar to that of the MMA-PA-AcM system (cf. Fig. 1).

Postpolymerization

From the DTA results shown in Figs. 4 and 5, it is possible to conclude that the MMA-PA-AcM system forms a glassy phase below $-104°C$ and a supercooled liquid phase between -104 and $-40°C$. In the MMA-SA-AcM and AN-SA-AcM systems, a glassy state is maintained below -75 and $-85°C$, respectively, and a supercooled liquid state is maintained between -75 and $-20°C$ and between -84 and $-34°C$, respectively.

In the course of cooling, these systems at a controlled rate, no thermal anomaly was found from $50°C$ to T_g; that is, crystallization does not occur and the systems form a supercooled liquid phase.

The postpolymerization of MMA in long-chain compound has been studied [6], but not in the supercooled liquid state.
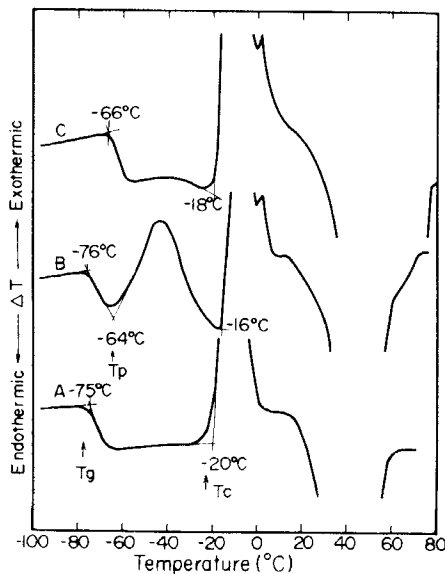
Fig. 8. DTA traces of methyl methacrylate-succinic acid-acetamide system.
A. Before irradiation. B. Irradiated (4×10^5 rad/hr $\times$ 1 hr at $-196°C$).
C. After B run. Heating rate: 0.2 mV/min.

Figure 7 shows that the postpolymerization of the MMA-PA-AcM system
(B) proceeds above T_g, and the starting temperature of postpolymerization
(T_p) is $-92°C$. The sample used for the B run was cooled down again to
$-140°C$ and used for the third DTA trace (C). In this case, T_g shifted to
$-98°C$, and no exothermic peak was observed in the range of the super-
cooled liquid phase. It is obvious that no polymerization occurred in the
temperature range from $-190°C$ to T_g.

The shift of T_g (from -104 to $-98°C$) was caused by a reduction in the
amount of MMA by polymerization (the polymer yield was ca. 30%), while
the polymer formed had a very weak influence on the thermal behavior of
the system. A similar observation was made in Fig. 8, namely, postpoly-
merization in the MMA-SA-AcM system (B) proceeded above T_g, where T_p
was $-64°C$ and T_c was $-16°C$.

The DTA trace (C) is almost the same as that of the SA-AcM system
(Fig. 5A). After the DTA measurement, the polymer yield reached ca.
90% in this case. The same tendency was observed in the DTA trace of
the AN-SA-AcM system; that is, polymerization occurred above T_g, where
T_p was $-75°C$ and T_c was $-18°C$. Polymer yield was ca. 70% in this case.
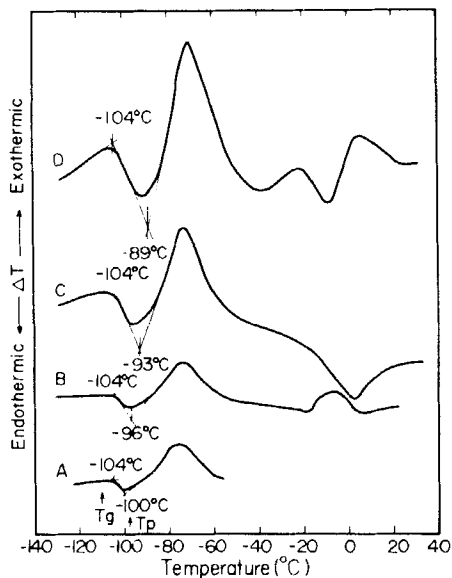
Fig. 9. DTA traces of methyl methacrylate-propionic acid-acetamide system irradiated. Heating rate, mV/min: A, 0.04; B, 0.1; C, 0.2; D, 0.4. Irradiation: 4×10^5 rad/hr $\times$ 1 hr at $-196°C$.
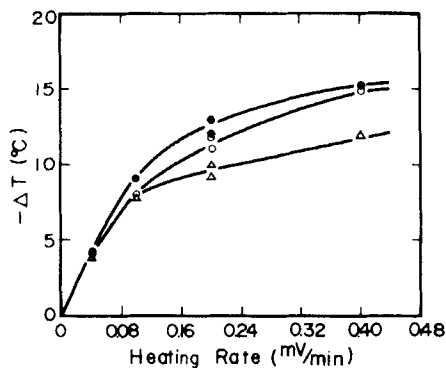

Fig. 10. Temperature difference (ΔT) between T_g and T_p as a function of heating rate. $\bigcirc$: Methyl methacrylate-propionic acid-acetamide. $\bullet$: Methyl methacrylate-succinic acid-acetamide. $\triangle$: Acrylonitrile-succinic acid-acetamide.
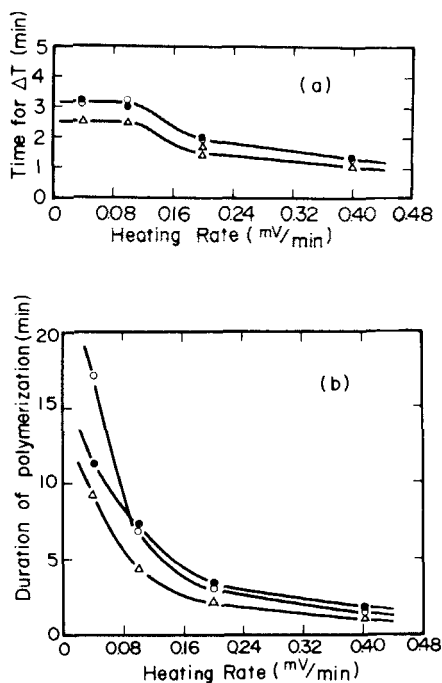
Fig. 11. Postpolymerization time as a function of heating rate. (a) Time from T_g to T_p vs. heating rate. (b) Time from T_p to the peak on the DTA traces vs. heating rate. O: Methyl methacrylate-propionic acid-adetamide. ●: Methyl methacrylate-succinic acid-acetamide. △: Acrylonitrile-succinic acid-acetamide.

From these results, it is concluded generally that the postpolymerization takes place just above T_g at a considerably high rate [4, 7]. In order to confirm this conclusion, the influence of heating rate on DTA traces was investigated as shown in Fig. 9, in which T_g does not change but T_p is shifted with increased heating rate. In the cases of the MMA-SA-AcM and AN-SA-AcM systems, the same tendency was observed.

Figure 10 shows the relation between the heating rate and the temperature interval from T_g to T_p ($\Delta T = T_g - T_p$). ΔT converges to 0, when the heating rate is extrapolated to 0.

This indicates that the postpolymerization should take place theoretically at T_g, that is, at the same time as the glass transition from a glassy phase to a supercooled liquid phase.
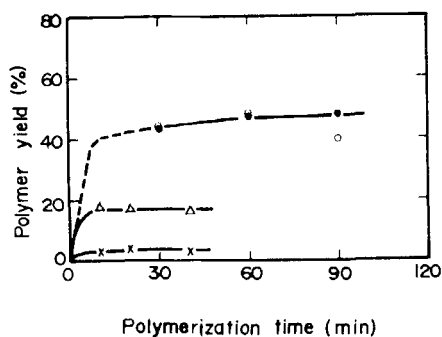
Fig. 12. Polymer yield as a function of postpolymerization time. Methyl methacrylate-propionic acid-acetamide system. Irradiation: 4×10^5 rad/hr $\times$ 1 hr at -196°C. Polymerization temperatures, °C: O, -78; •, -70; $\triangle$, -48; $\times$, 25.
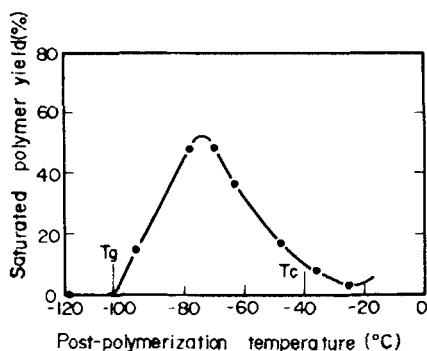

Fig. 13. Saturated polymer yield as a function of postpolymerization temperature. Methyl methacrylate-propionic acid-acetamide system. Irradiation: 4×10^5 rad/hr $\times$ 1 hr at -196°C. Postpolymerization time: 1 hr.

Figure 11a shows that the time taken for heating up from T_g to T_p is quite short (less than 3 min) for three cases.

Figure 11b shows that the duration of polymerization reaction decreases with increasing heating rate. At a higher heating rate, the postpolymerization reaction is finished within a few minutes.

In parallel, a kinetic study of the postpolymerization was carried out. The results are shown in Fig. 12. The polymer yield was saturated after 10 min.
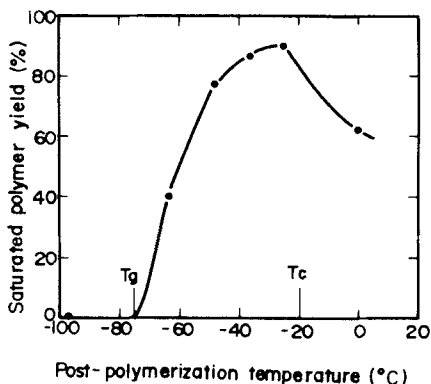
Fig. 14. Saturated polymer yield as a function of polymerization tempera-
ture. Methyl methacrylate-succinic acid-acetamide system. Irradiation:
4×10^5 rad/hr $\times$ 1 hr at $-196°C$. Postpolymerization time: 1 hr.
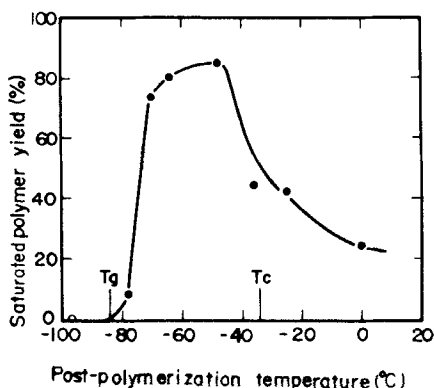

Fig. 15. Saturated polymer yield as a function of polymerization tempera-
ture. Acrylonitrile-succinic acid-acetamide system. Irradiation: 4×10^5
rad/hr $\times$ 1 hr at $-196°C$. Postpolymerization time: 1 hr.

This saturated polymer yield varied as a function of polymerization tem-
perature, as indicated in Figs. 13-15. In all systems, an apparent maximum
value was found between T_g and T_c, as in the case of in-source polymeri-
zation. T_c was not observed in the case of in-source polymerization, while
in the case of postpolymerization the system had T_c.

Below T_g the NMR spectra are composed of a large amount of broad

Table 2. Molecular Weights of Polymers Obtained in the Postpolymerization of the Methyl Methacrylate-Propionic acid-Acetamide System[a]

Polymerization time, min[b]	(A)		Polymerization temperature, °C[c]	(B)	
	$[\eta]$	$Mn \times 10^{-5}$		$[\eta]$	$Mn \times 10^{-5}$
30	0.38	0.76	-97 (in vacuo)	0.30	0.56
60	0.42	0.87	-78 "	0.46	0.98
90	0.46	0.98	-70 "	0.42	0.87
			-39 "	0.16	0.24
			-20 "	0.33	0.63

[a]Composition, mole %: MMA, 13; PA, 38; AcM, 49. Irradiation: 4 × 10⁵ rad/hr × 1 hr at -196°C.

[b]Polymerization at -70°C in vacuo.

[c]Polymerization for 1 hr.

component (peak-to-peak width (ΔH) = 10.5 G) and a small amount of narrow component (ΔH = 1.5 G). However, above T_g the spectra are changed to a small amount of broad component (ΔH = 7.6 G) and a large amount of narrow component (ΔH = 0.4 G). Above T_c the spectra become very narrow (ΔH < 0.1 G). That is, the movement of molecules is quite different below and above T_g.

The mechanism of postpolymerization is the same as that explained above.

Table 2(A) shows that the molecular weights of the polymers obtained in Fig. 12 increase with polymerization time. Table 2(B) shows the molecular weights of the polymers obtained in Fig. 13 as a function of polymerization temperature.
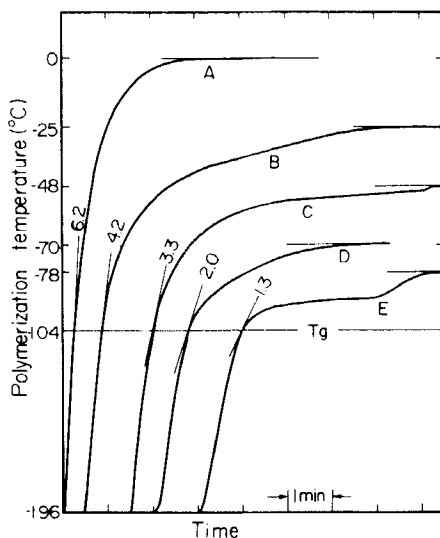

Fig. 16. Thermograms of the polymerization system. Methyl methacrylate-propionic acid-acetamide system. From $-196°C$ to: A, $0°C$; B, $-25°C$; C, $-48°C$; D, $-70°C$; E, $-78°C$. The figures in the diagram indicate heating rate (mV/min) at T_g.

In the case of the kinetic study of postpolymerization, the inner temperature of the system was measured directly with an iron-constantan thermocouple. The ampoule was kept at $-196°C$ at first, and then immersed into a Dewer vessel at desired temperature. The results are

shown in Fig. 16. From these results, it is possible to estimate the heating rate when the temperature of an ampoule passes through T_g; that is, the heating rate is 6.2 mV/min when the ampoule at $-196°C$ is immersed into a vessel at $0°C$, and 1.3 mV/min when immersed at $-78°C$. In all cases, the heating rate is very fast at T_g.

From Fig. 11, it is obvious that the postpolymerization reaction was completed instantly at T_g. This means that the rate of heat transfer from the outside vessel to the inner sample plays an important role in polymerization.

In the case of postpolymerization in a supercooled liquid phase, especially in the system in which monomer is dissolved into a non-polymerizable glassy matrix, the rate of heat transfer into the sample determines the polymer yield.

In these systems an increase in sample temperature accelerates the polymerization reaction rate, mainly due to the accumulation of heat of polymerization.

Careful attention should be given to handling and heating up the sample after irradiation.

ACKNOWLEDGMENT

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