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Radiation-Induced Polymerization of Methyl Methacrylate at High Pressure

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ABSTRACT

Radiation-induced polymerization of methyl methacrylate (MMA) was studied up to 7500 kg/cm^2 at 20°C. The rate of polymerization increased to 3000 kg/cm^2 with overall activation volume $\Delta V_{pol}^{\ddagger}$ of -23.6 cm^3/mole, and then the pressure dependence of the rate was very small in the pressure range between 3000 and 3700 kg/cm^2. The rate of polymerization increased again above 3700 kg/cm^2 up to the crystallization pressure of MMA (5500 kg/cm^2) with $\Delta V_{pol}^{\ddagger}$ of -13.7 cm^3/mole with increasing pressure. The volume contraction by polymerization decreased with increasing pressure up to 3000 kg/cm^2 but hardly decreased with increasing pressure above 3000 kg/cm^2. The stereoregularity (triad probability) of PMMA changed slightly at 3000 kg/cm^2; above 3000 kg/cm^2, syndiotactic addition decreased and heterotactic addition increased. Marked change in P-V isotherms of MMA, however, was not observed about 3000 kg/cm^2. We concluded from these facts that an alignment of monomer molecules, which does not cause large volume change, was realized about 3000 kg/cm^2. Polymerization proceeded above the crystallization pressure by long time irradiation, and isotactic addition increased clearly in the solid-state polymerization.

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INTRODUCTION

It has been reported that activation entropy $\Delta S^{\ddagger}$ decreases with increasing pressure in polymerization at high pressure [1, 2]. This suggests that an alignment of monomer molecules is realized by compression. Osugi et al. have suggested that an alignment of monomer molecules exists in the polymerization of acetaldehyde at high pressure [3].

In order to elucidate the alignment of monomer molecules at high pressure, methyl methacrylate (MMA) is considered to be a convenient monomer because polymerization at high pressure of MMA has been studied by many researchers [4-7]. MMA is expected to align more easily than molecules of complex structure, because MMA consists of planar units [$H_2C{=}C(CH_3)R$, $>C{=}O$].

The radiation-induced polymerization has advantages in study of the initial rate without disturbance during heating and pressurization, since the polymerization can be started by γ-irradiation after the polymerization conditions have been established.

We studied radiation-induced polymerization of MMA at high pressure by using dilatometry as a first step in elucidating the correlation between the features of polymerization and properties of the monomer at high pressure.

EXPERIMENTAL

Polymerization was carried out in a glass dilatometer with about a 2-cm^3 monomer cell (Fig. 1).

Freshly distilled MMA was introduced into the monomer cell, and the monomer cell was joined to the capillary in the inverted position as shown in Fig. 1. The monomer was degassed by the freeze-thaw method several times (at $\sim 10^{-3}$ Torr) on a vacuum line, then mercury was introduced under vacuum and the monomer cell was turned to the position as shown in Fig. 1. The application of pressure to the dilatometer was carried out hydrostatically by using the high pressure apparatus reported elsewhere [8]. The electric leads from the platinum wire exited through the plug of the high pressure vessel. The change in electric resistance of platinum wire caused by change of mercury level in the capillary was detected as a change in voltage (ΔE) at constant current (20 mA).

Polymerization was carried out at 20°C with Co-60 γ-rays at dose rate of 7×10^3 rad/hr (for Frike solution).

By assuming a proportionality between the dilatometric reading ΔE and the monomer conversion in the present experimental range, the monomer conversion can be calculated from ΔE if the ratio

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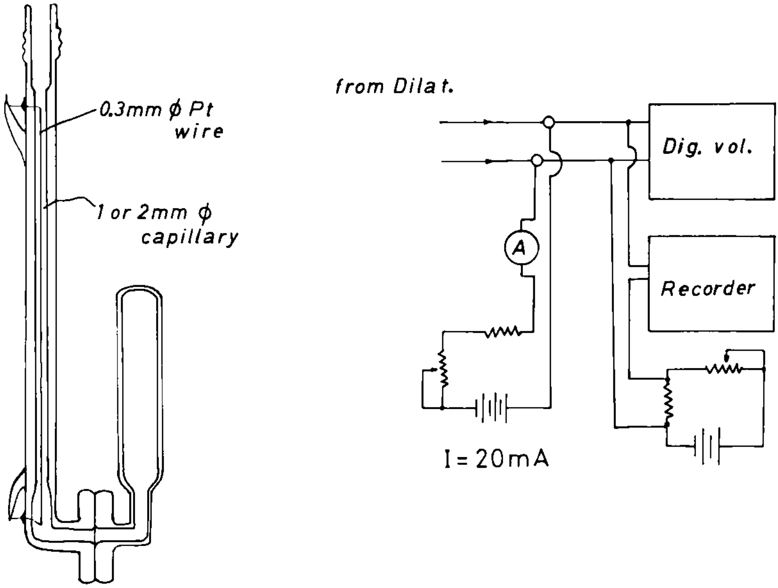

FIG. 1. Section of dilatometer and electric circuit.

(final conversion/final ΔE) is determined. The final conversion of MMA to PMMA was determined gravimetrically after vacuum drying.

Calculation of specific volume from the relation between ΔE and pressure was carried out by the same method reported previously [9].

RESULTS

Figure 2 shows the pressure-volume (P-V) isotherm of MMA obtained at pressurization rate of about 50 kg/cm^2/min at 20°C. The specific volume decreases smoothly with increasing pressure up to 5600 kg/cm^2. The specific volume decreases abruptly at 5600 kg/cm^2 with elevating pressure, and increases abruptly at 4500 kg/cm^2 with pressure decreasing from higher pressure than 5600 kg/cm^2. MMA is known to be crystallized at -47°C at atmospheric pressure, so that MMA crystallizes at about 5000 kg/cm^2 and is in a supercooled liquid state in the pressure range between 5000 and 5600 kg/cm^2 with rising pressure.

Figure 3 shows the time-conversion curve at 4500 kg/cm^2 at

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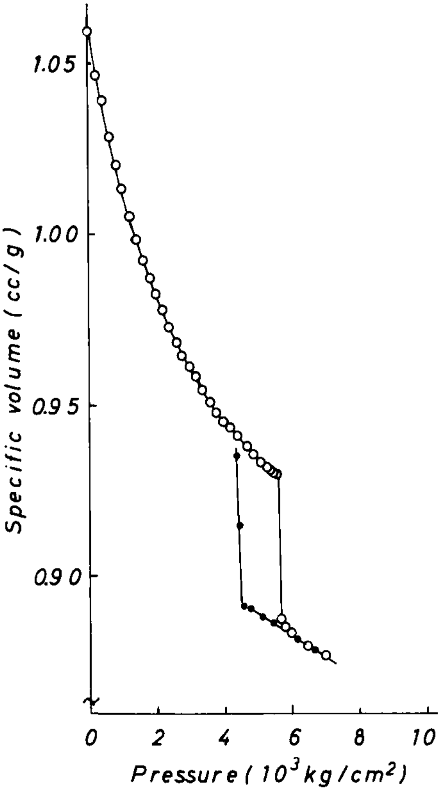

FIG. 2. P-V isotherm of MMA: (o) measurement with increasing pressure; (•) measurement with decreasing pressure.

20°C. The filled circles are monomer conversions obtained by gravimetry at different polymerization times and the solid line is the time-conversion curve obtained by dilatometry normalized to polymer yield for the longest polymerization time (22 min). Since the time-conversion curves obtained by the two methods are in agreement with each other, the rate of polymerization was thereafter analyzed only dilatometrically.

Figure 4 shows the time-conversion curves at various pressures at 20°C. Polymerization proceeds autocatalytically after a short induction period, and the rate of polymerization increases with increasing pressure up to 5300 kg/cm^2. The acceleration in the rate of polymerization at a later stage may be due to a decrease in the rate of termination and radical accumulation due to an increase in

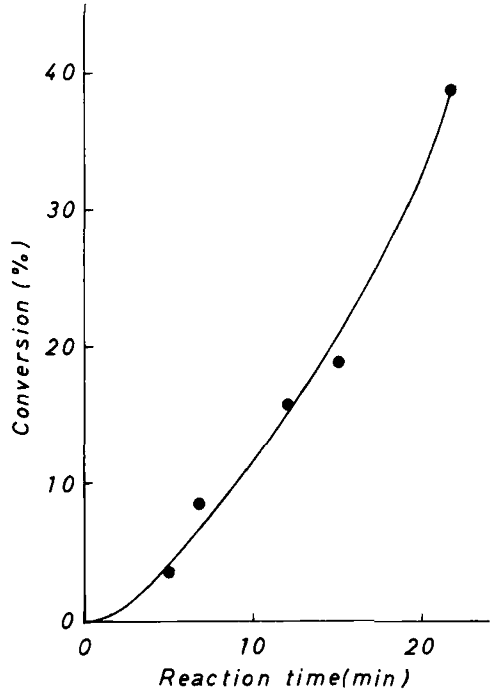

FIG. 3. Typical time-conversion curve at 4000 kg/cm^2, 20°C; (—) from dilatometry, (●) from gravimetry.

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viscosity. At 5300 kg/cm^2, where MMA is in a supercooled liquid state, the polymerization proceeds. The dilatometric data during polymerization in the supercooled state is sensitively affected by fluctuation of pressure and temperature. The time conversion curve at 5300 kg/cm^2 shown in Fig. 4 is an example in which the polymerization proceeds to high conversion. Typical dilatometric data for the supercooled liquid state are shown in Fig. 5, in which the polymerization proceeds autocatalytically for a few minutes, the volume decreases abruptly, and then the volume scarcely changes. This abrupt volume change is not to polymerization but due to a phase change of the polymeric system. An accumulation of polymer chains is considered to trigger solidification of the polymeric system.

Above the crystallization pressure, polymerization does not occur within the time scale of present experiments, but polymerization proceeds in high conversion on long-time irradiation (ca. 73% at 7500 kg/cm^2 for 65 hr). Polymerization in the crystalline state

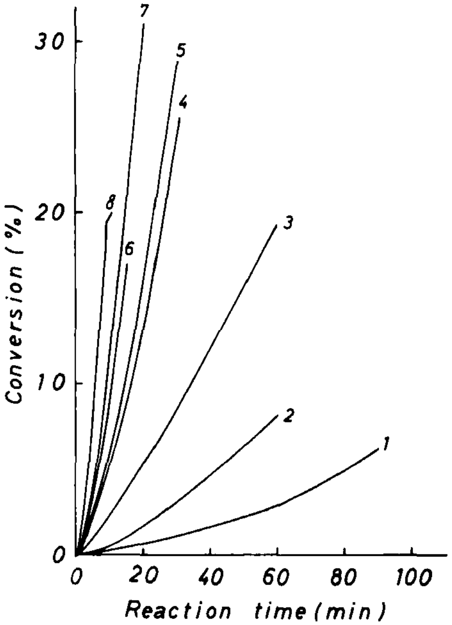

FIG. 4. Time-conversion curves at various pressures at 20°C: (1) 1000, (2) 1600, (3) 2300, (4) 3000, (5) 3700, (6) 4000, (7) 4500, (8) 5300 kg/cm^2.

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may proceed around defects of the monomer crystals and the defects produced by polymer formation.

The initial rate of polymerization just after the induction period is plotted on a logarithmic scale against pressure in Fig. 6 (Van't Hoff plot). The overall activation volume $\Delta V^{\ddagger}_{\text{pol}}$ calculated from linear part up to 3000 kg/cm^2 is -23.6 cm^3/mole. In the pressure range of 3000 to 3700 kg/cm^2, dependence of the rate of polymerization on pressure is small. The Van't Hoff plot is again linear above 4000 kg/cm^2, and the $\Delta V^{\ddagger}_{\text{pol}}$ is -13.7 cm^3/mole.

Figure 7 shows the volume contraction by polymerization in the initial stage at various pressures together with P-V isotherms of MMA at 20°C. The pressure dependence of the volume contraction by polymerization decreases above 3000 kg/cm^2 in spite of the absence of a marked change in P-V isotherm of MMA around 3000 kg/cm^2.

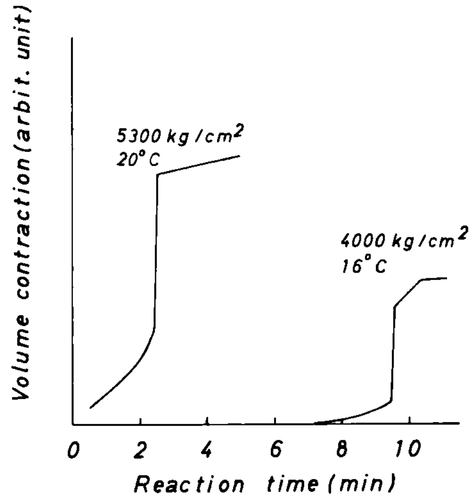

FIG. 5. Typical dilatometric curves in polymerization in a supercooled state; conversions are 7.8% and 4.1% at 5300 kg/cm^2, 20°C and 4000 kg/cm^2, 16°C, respectively.

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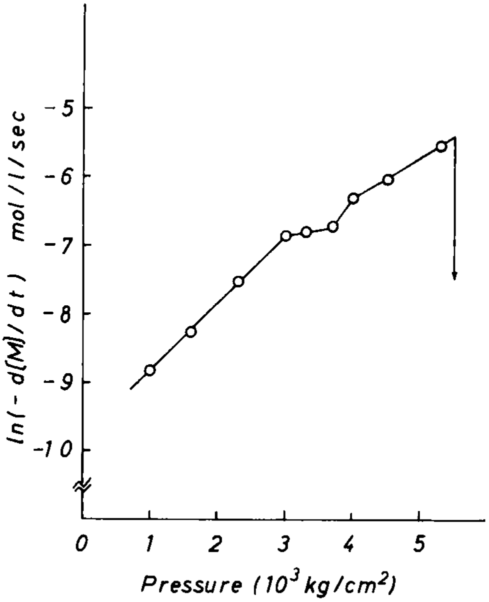

FIG. 6. Van't Hoff plot at 20°C.

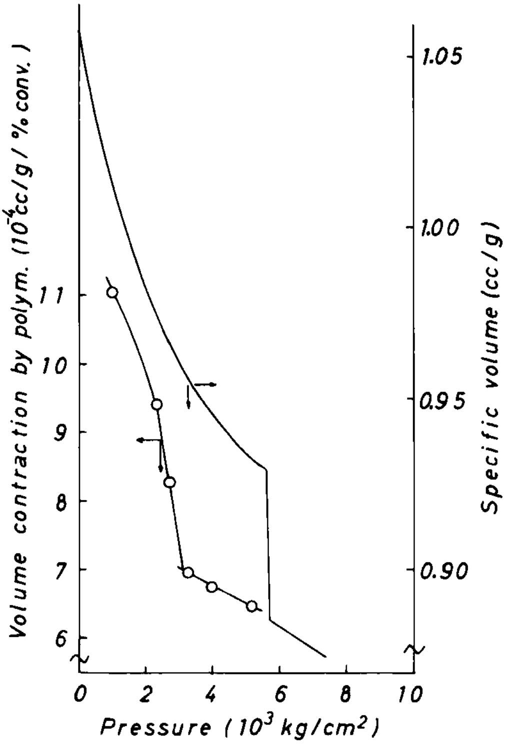

FIG. 7. Volume contraction by polymerization and P-V isotherm of MMA at 20°C.

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DISCUSSION

Activation Volume

Asai et al. [1] have reported that $\Delta V^{\ddagger}_{pol}$ in AIBN-initiated polymerization of MMA up to 1000 kg/cm^2 is -17.3 cm^3/mole at 40°C and the $\Delta V^{\ddagger}_{pol}$ increases with elevating temperature. The value of $\Delta V^{\ddagger}_{pol}$ extrapolated from Asai's data is about -14 cm^3/mole at 20°C. This value differs from the $\Delta V^{\ddagger}_{pol}$ below 3000 kg/cm^2 (-23.6 cm^3/mole) in this work. The inconsistency in $\Delta V^{\ddagger}_{pol}$ is due to the difference in the activation volume of initiation $\Delta V_i^{\ddagger}$ between radiation-induced *reaction and AIBN-initiated reaction.* The $\Delta V^\ddagger$ of AIBN decomposition measured by optical absorption of AIBN is 3.8 cm^3/mole, while the $\Delta V^\ddagger$ measured by I_2 scavenging is 9.4 cm^3/mole [10]. We think $\Delta V^\ddagger$ by I_2 scavenging is applicable to $\Delta V_i^\ddagger$ of AIBN-initiated polymerization, because diffusion of the radicals out of the cage must be necessary for both scavenging by I_2 and initiating polymerization. If $\Delta V^\ddagger$ of initiation of AIBN is 9.4 cm^3/mole, the value of $\Delta V^\ddagger_{pol}$ in this work agrees with the $\Delta V^\ddagger_{pol}$ in Asai's experiment.

Monomer Alignment above 3000 kg/cm²

The overall activation volume in radiation-induced vinyl polymerization $\Delta V^\ddagger_{pol}$ is divided as follows;

$$\Delta V^\ddagger_{pol} = \Delta V^\ddagger_p + n\Delta V_i^\ddagger - n\Delta V_t^\ddagger$$

where n = 0.5 - 1, and where $\Delta V_p^\ddagger$, $\Delta V_i^\ddagger$, and $\Delta V_t^\ddagger$ are activation volumes of propagation, initiation, and termination, respectively. In general, $\Delta V_t^\ddagger$ is positive due to the increase in the viscosity at high pressure [11] and $\Delta V_i^\ddagger$ may be positive, since radical formation is formation of two molecules from one molecule. When the magnitudes of $\Delta V_i^\ddagger$ and $\Delta V_t^\ddagger$ are comparable, $\Delta V^\ddagger_{pol}$ is nearly equal to $\Delta V_p^\ddagger$.

The contraction of distance along the molecular axis between monomer and polymer radical from original state to the activated state can be calculated by using the cross section of MMA and $\Delta V^\ddagger_{pol}$. The cross section of MMA is estimated by the method shown in the Appendix, and this value is 19.4 Å^2 at atmospheric pressure. Since $\Delta V^\ddagger_{pol}$ is -23.6 cm^3/mole below 3000 kg/cm^2, the contraction of the distance is calculated to be 2.3 Å; on the contrary, the contraction of the distance is 1.4 Å above 4000 kg/cm^2 assuming that the cross section of monomer is 19.4 Å^2. As the activated complex also has compressibility and the cross section of monomer at high pressure differs from that at atmospheric pressure, the real contraction of the distance at high pressure may be larger than the calculated value. The contraction of the distance in the transition above 3700 kg/cm^2 is clearly reduced relative to that below 3000 kg/cm^2, suggesting that the monomer system is in fairly limited alignment, which is similar to molecule packing of that in the activated state.

The volume contraction by polymerization above 3000 kg/cm^2 hardly depends on pressure. This fact also suggests that the monomer

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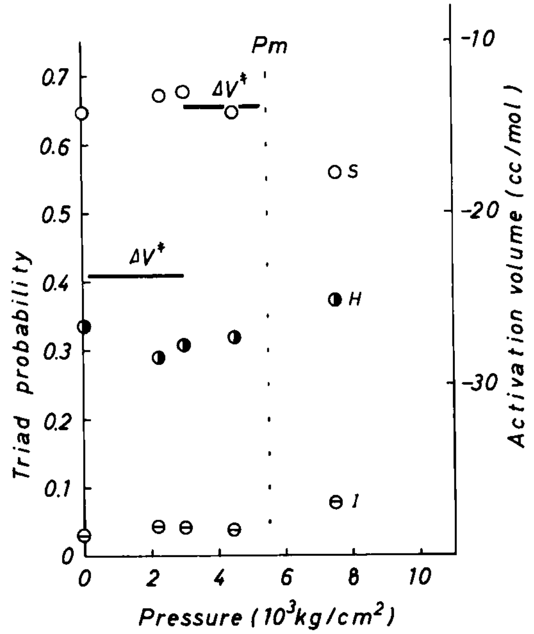

FIG. 8. Triad probability of PMMA polymerized at various pressures and activation volume of polymerization of MMA: (S) syndiotactic; (H) heterotactic; (I) isotactic.

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molecule packing is similar to the activated state and the polymer. The entropy of the system is fully decreased above 3000 kg/cm^2 at 20°C. The monomer system, however, does not have a long-range order, even above 3000 kg/cm^2, because the P-V relation of MMA does not show a marked change about 3000 kg/cm^2. It is concluded that a cluster of monomer molecules with short-range order is dispersed in a sea of random monomer.

Figure 8 shows the triad probability of PMMA obtained by NMR measurement against pressure. For PMMA polymerized above the crystallization pressure, syndiotactic addition decreases and isotactic addition increases, because the propagation proceeds near the complete aligned monomer molecules in crystal lattice. Below the crystallization pressure the change in tacticity with pressure is small, but above 3000 kg/cm^2 syndiotactic addition tends to decrease and heterotactic addition tends to increase. A change in tacticity at high pressure has been reported [7, 12]. Walling et al. have concluded that the transient state for syndiotactic addition is slightly larger than that for isotactic addition to the growing chain. The increase in lll and ddd addition at high pressure also shows that the monomer molecules are aligned in fairly limited molecular packing. However, the fact that pressure does not induce a marked change in tacticity is proof that the monomer system does not have long-range order.

The unusual feature of the Van't Hoff plot at 3000 to 3700 kg/cm^2 (Fig. 6) is considered to be the transient state in molecular packing. We concluded from this discussion that clusters of MMA having short-range order are dispersed in random MMA above 3000 kg/cm^2.

APPENDIX

The molecular shape of MMA estimated from length of atomic bonding and van der Waal's radii is shown in Fig. 9. The $H_2C{=}C(CH_3)R$ and $-\underset{\underset{O}{\|}}{C}-O$ groups are planar. Though bonds a and b are rotatable,

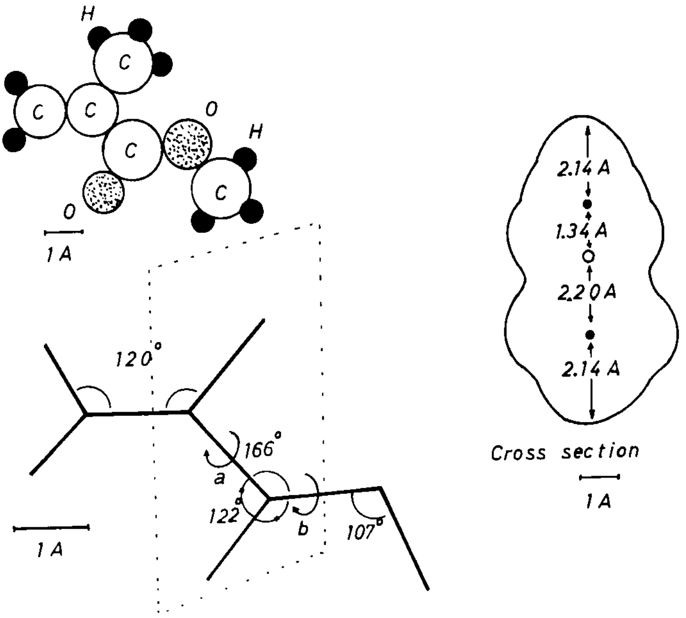

FIG. 9. Molecular model and cross section of MMA.

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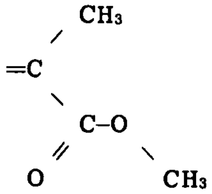
these bonds cannot rotate freely due to steric hindrance of the CH_3 group. Therefore, MMA is a planar structure.

If the monomer located next to the growing radical is separated by the van der Waal's radii (4 Å) distance along the monomer axis of the polymer chain before addition, the decrement along molecular axis by one monomer addition is 2.25 Å, since the C–C bond length is 1.54 A, and the change from C=C to C–C is 0.21 Å (4 - 1.54 - 0.21 = 2.25). If the volume contraction due to polymerization determined only by the change in the length, the cross section of MMA at atmospheric pressure can be calculated from densities of the monomer and polymer. Since the volume contraction at atmospheric pressure at 20°C calculated from MMA and PMMA densities is 21.5 cm^3/mole, the cross section of MMA is calculated to be

$$\frac{21.5/(2.25 \times 10^{-8}/\sin 55^\circ)}{6 \times 10^{23}} = 19.4\ \text{A}^2$$

where 6×10^{23} and sin 55° are Avogadro's number and correction of half of the C–C–C bond angle. The real cross section may be larger, since the polymer is in the glassy state at 20°C. The cross section of MMA calculated from the illustration in Fig. 9 by using the bond length and van der Waal's radii is 23.9 Å^2, when



is planar. The cross section of 19.4 Å^2 is used for calculation of the contraction of distance in the transition state.

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REFERENCES

[1] H. Asai and T. Imoto, Nippon Kagaku Zasshi, 84, 863 (1963).

[2] H. Nakamoto, Y. Ogo, and T. Imoto, Makromol. Chem., 111, (1968).

[3] J. Osugi and T. Mizukami, Nippon Kagaku Zasshi, 87, 1157 (1966).

[4] L. F. Vereschagin, V. A. Derevitskaya, and S. A. Rogovin, Zh. Fiz. Khim., 21, 233 (1947).

[5] E. V. Melekhina and E. V. Kuvshinskii, Zh. Fiz. Khim., 32, 1061 (1958).

[6] V. P. Aubov, V. A. Kargin, and A. A. Shchetinin, Vyskomol. Soedin., 2, 1722 (1960).

[7] H. Asai and T. Imoto, Nippon Kagaku Zasshi, 84, 871 (1963).

[8] T. Sasuga, N. Morishita, A. Udagawa, Y. Kusama, and M. Takehisa, J. Polym. Sci. Polym. Chem. Ed., 14, 2575 (1976).

[9] T. Sasuga and M. Takehisa, J. Macromol. Sci.–Phys. B13, 251 (1977).

[10] A. H. Ewald, Discussions Faraday Soc., 22, 138 (1956).

[11] A. E. Nicholson and R. G. W. Norrish, Discussions Faraday Soc., 22, 67, 104 (1956).

[12] C. Walling and D. D. Tanner, J. Polym. Sci. A, 1, 2271 (1963).

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