

Effect of Methanol On Optical Property of Irradiated Poly(Methyl Methacrylate)

C. B. LIN and SANBOH LEE*

Department of Materials Science, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

SYNOPSIS

The effect of methanol on optical property of irradiated poly(methyl methacrylate) (PMMA) has been investigated. The gamma irradiation enhances the methanol transport in PMMA. The activation energies of diffusivity for case I and velocity for case II decreases with increasing gamma ray dose. For the same wavelength, in the range 350–800 nm, the transmittance decreases with increasing gamma ray dose. The equation of transmittance I with gamma ray dose ϕ at the wavelength 405 nm is $I = I_0 \exp(-0.06\phi^{1/2})$, where I_0 is the transmittance of virgin PMMA. When the irradiated PMMA is immersed into methanol bath, the yellow color fades out gradually. The recovery of transmittance increases with methanol content in irradiated PMMA. The boundary to separate the outer region (solvent-affected zone) from the inner region (no solvent-affected zone) is also studied. The rate of boundary movement increases with gamma ray dose.

INTRODUCTION

It is known that when polymeric materials are exposed to high-energy radiation either crosslinks or scissions are observed.^{1–3} The former leads to an increase in molecular weight and the latter has the opposite trend. For example, polyethylene crosslinks and poly(methyl methacrylate) (PMMA) scissions. Thus, the effect of gamma ray radiation on PMMA scissions has been extensively studied. For example, Wall and Brown⁴ determined the number of scissions of PMMA arising from gamma ray radiation by the intrinsic viscosity measurement. Ouano et al.⁵ measured the molecular weight distribution of PMMA due to gamma irradiation by the technique of gel-permeation chromatography. Pratt⁶ confirmed that the glass transition temperature of irradiated PMMA is inversely proportional to the average molecular weight. The molecular weight distribution of PMMA under the influence of high-energy radiation was also studied by Shultz et al.⁷ using light scattering.

The effect of gamma irradiation on the different properties of PMMA has also been paid much at-

ention. For example, Subrahmanyam and Subrahmanyam⁸ studied thermal expansion and specific heat using a three-terminal capacitance technique. Color variation of radiation dosage was observed by Knappe and Yamamoto.⁹ Volatile products from gamma irradiation of PMMA were found by Todd¹⁰ and David et al.¹¹ Ohnishi and Nitta¹² reported the rate of formation of the free radicals in PMMA by gamma irradiation using ESR absorption. Using gamma irradiation of PMMA, Kusy and Katz¹³ measured fracture surface energy as a function of viscosity average molecular weight.

Turner¹⁴ concluded that the uptake of water up to 2.0 w % depends on the dosage of gamma irradiation of PMMA. The effect of plasticizer on water sorption was also investigated by Kalachandra and Turner.¹⁵ Harmon et al.^{16,17} studied methanol transport in deformed crosslinked PMMA. Recently, Lin et al.¹⁸ reported methanol-induced crack healing in PMMA. These observations prompted us to study methanol transport and related optical properties in irradiated PMMA.

EXPERIMENTAL

The present work involves determinations of intrinsic viscosity, glass transition temperature, ab-

* To whom correspondence should be addressed.

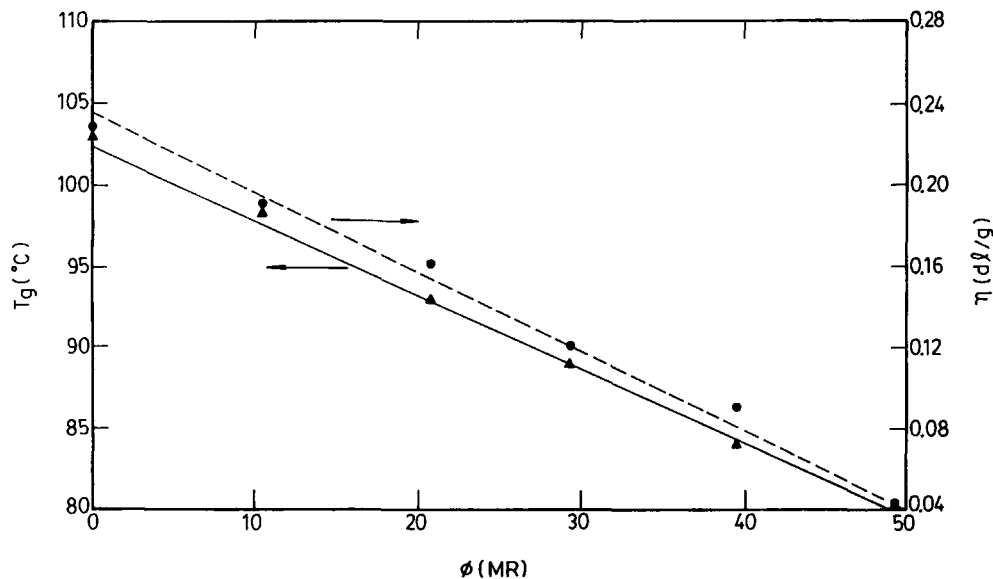


Figure 1 T_g and intrinsic viscosity of PMMA as a function of gamma ray dose.

sorption, and optical transmittance of irradiated PMMA. The initial stages of specimen preparation were similar for studies of all four of these properties. PMMA with inherent viscosity 0.237 dL/g was obtained from Du Pont in the form of a type-L Lucite cast acrylic sheet of thickness 6.35 mm. All specimens, excepting for the glass transition temperature

measurement, were initially prepared as follows. Specimens of $20 \times 6.35 \times 1.0$ mm were cut from the sheet and polished using 600- and 1000-grid carbimet papers, followed by final polishing with 1- and 0.05- μm alumina slurries. Prior to gamma ray radiation, the specimens were annealed in air for 24 h at 120°C and then furnace cooled to the ambient temperature,

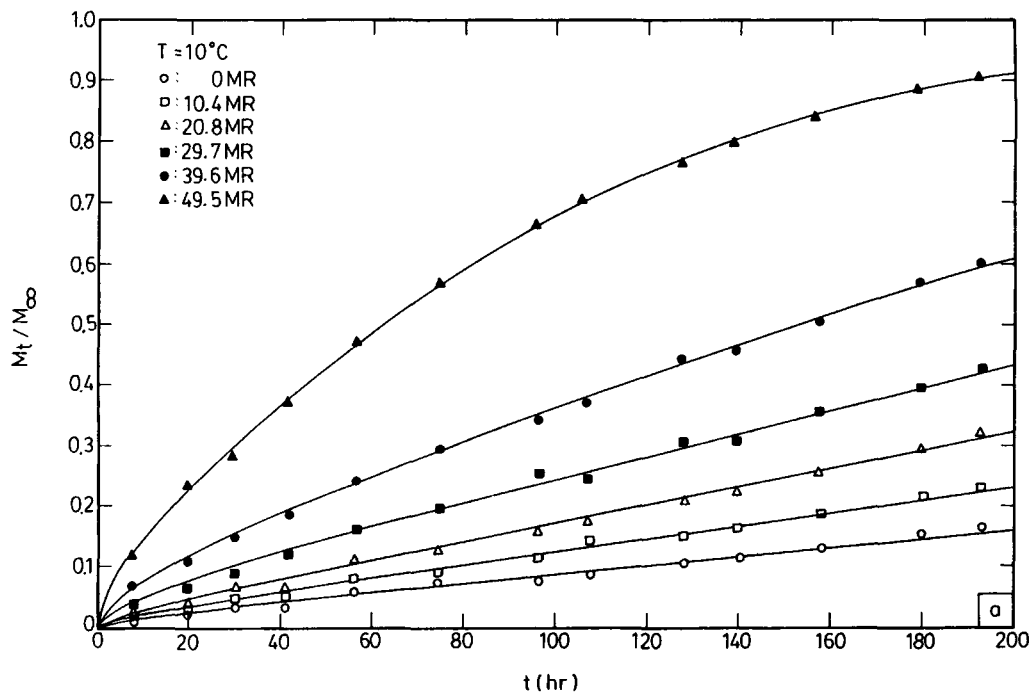


Figure 2 Methanol absorption in irradiated PMMA. (a), $T = 10^{\circ}\text{C}$; (b), $T = 14^{\circ}\text{C}$; (c), $T = 18^{\circ}\text{C}$; (d), $T = 22^{\circ}\text{C}$; (e), $T = 26^{\circ}\text{C}$.

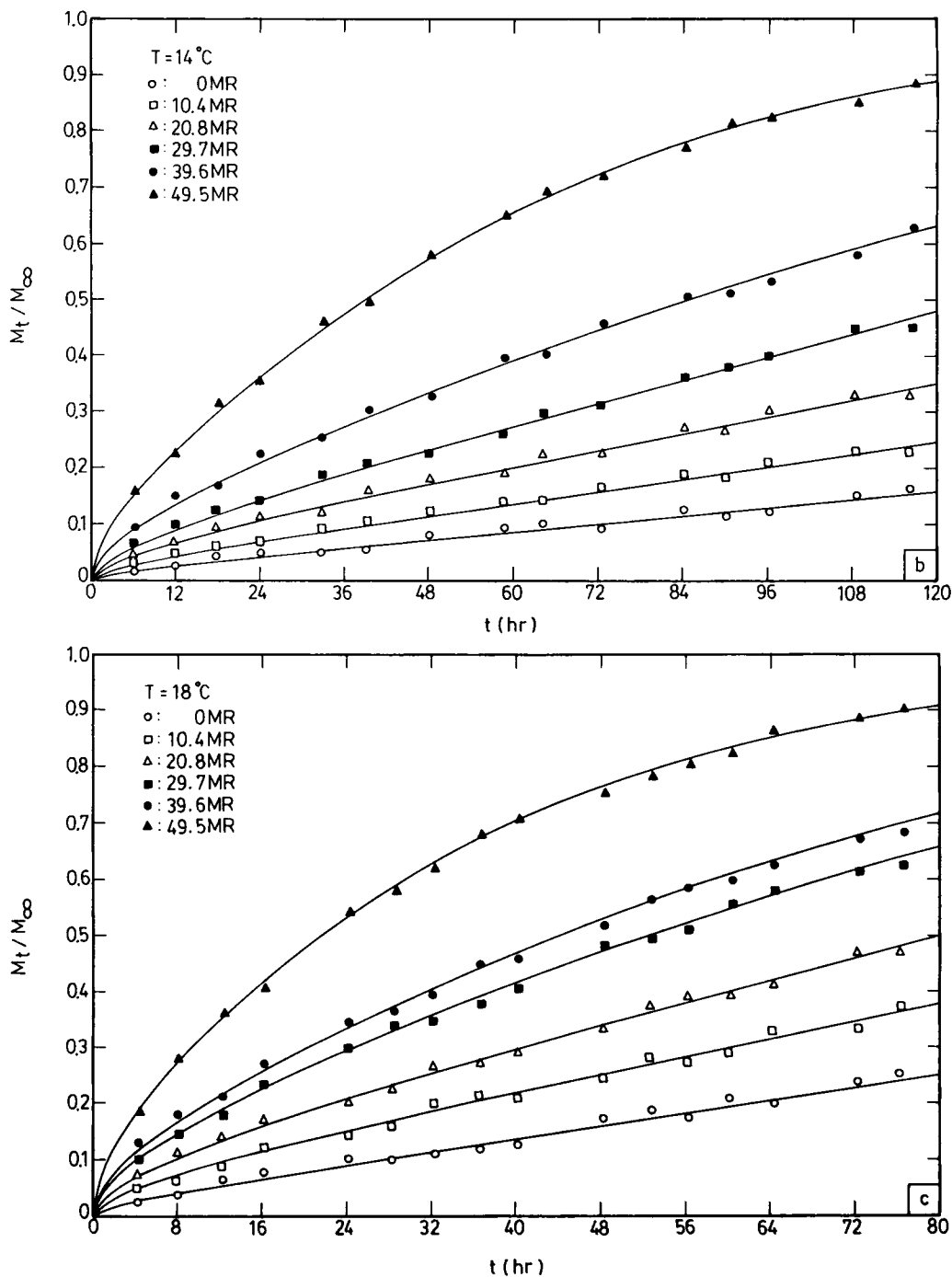


Figure 2 (continued from the previous page)

approximately 26°C . The specimens were exposed in air to gamma ray from a Co-60 source with the dose rate 1 MR/h at ambient temperature.

Intrinsic Viscosity and T_g

The intrinsic viscosity specimen was dissolved in acetone of 0.5 g/dL at ambient temperature. The

intrinsic viscosity was measured using the Ubbelohde capillary viscometer in the thermostatted water bath maintained at $(25 \pm 0.1)^\circ\text{C}$. Glass transition temperature specimens were produced by cutting a layer of thickness approximately 0.3 mm from the cast sheet and then, after polished, punching out disks of 8 mm diameter. Resulting disks were annealed at 120°C for 24 h. Then a disk of roughly

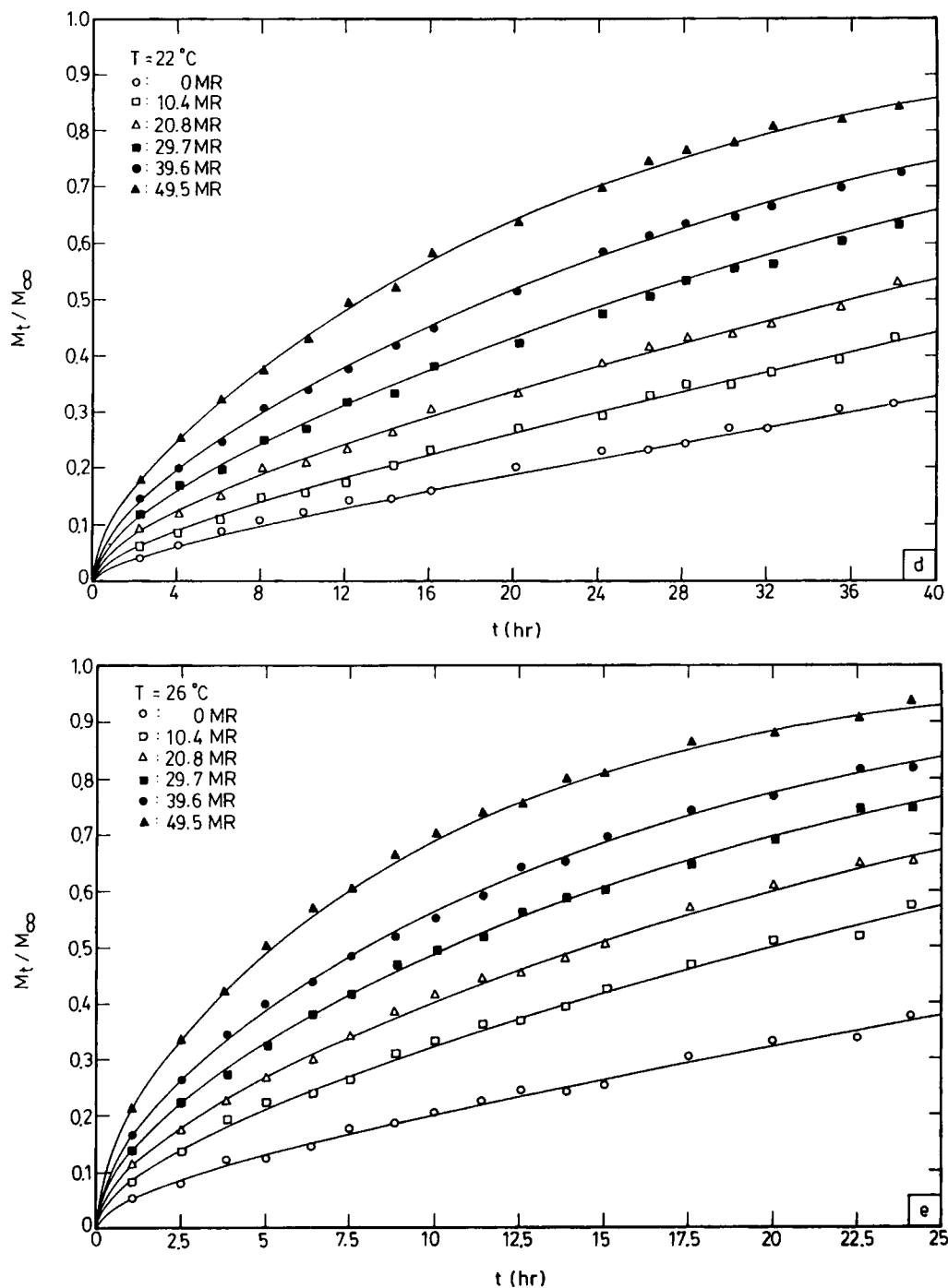


Figure 2 (continued from the previous page)

10 mg was exposed in air to gamma ray for different time to reach the desired dose. Each specimen was enclosed in a regular aluminum pan and moved into a SEIKO 1 SSC-500 differential scanning calorimeter for measurement at scanning rate $5^\circ\text{C}/\text{min}$. The specimen was heated from the ambient temperature to 105°C with a heating rate of $2^\circ\text{C}/\text{min}$.

Absorption Study

Each absorption study specimen was preweighed. Time of specimen exposed to gamma ray was the same as in the intrinsic viscosity and glass transition temperature studies. Then the specimen was pre-cooled in a thermostatted water bath to experimental

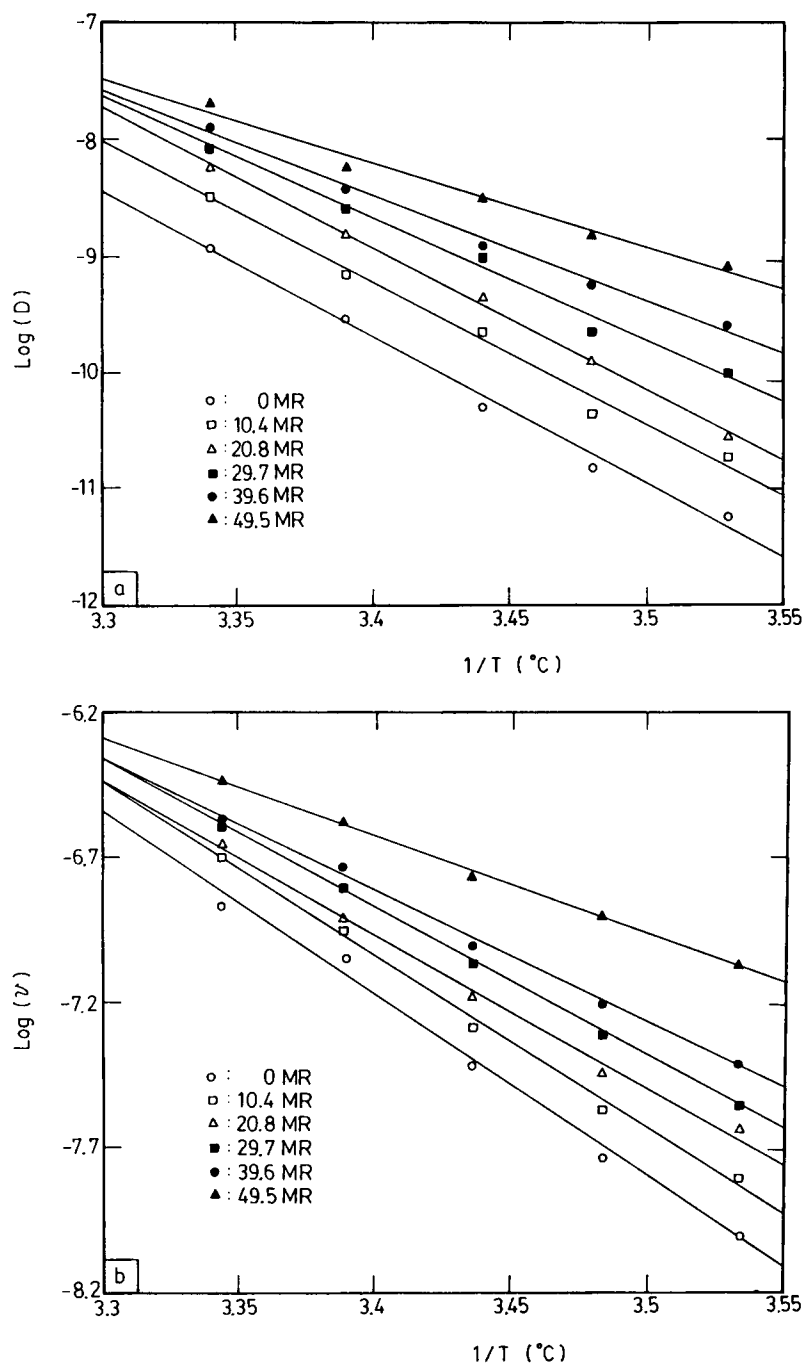


Figure 3 Plot of (a) $\text{Log}(D)$ and (b) $\text{Log}(v)$ as a function of $(1/T)$. The units of D and v are cm^2/s and cm/s , respectively.

temperature and moved to a methanol-filled glass bottle at the same temperature, maintained by means of a thermostatted water bath. After each experimental interval of immersion, the specimen was removed, its surfaces blotted free of surplus methanol, and its mass measured using a Kern 870 digital balance. After being weighed, the specimen was dropped out because of crack nucleation.

Transmittance Study

Each transmittance specimen was cooled and periods for specimen exposed to gamma ray and immersed in methanol are exact as in the absorption study. Transmittance was conducted using a Hitachi U-3210/U-3240 spectrometer in the range of wavelength 350–800 nm. The penetrant front of methanol

in irradiated specimen was observed using a Leitz Metallux 3 optical microscope.

RESULTS AND DISCUSSION

The glass transition temperature T_g of irradiated PMMA decreases with the increasing radiation dosage as shown in Figure 1 by a solid line. Although the glass transition temperature reported by Pratt⁶ was slightly higher than ours, both trends of T_g vs. dosage ϕ are similar. The intrinsic viscosity η as a function of dosage is also plotted in Figure 1 by a broken line. The intrinsic viscosity decreases with the increasing dosage, which is consistent with that observed by Wall and Brown.⁴ Both measurements of glass transition temperature and intrinsic viscosity confirm that the decrease of molecular weight of PMMA arises from the gamma irradiation.

Methanol Transport

The data of methanol transport in irradiated PMMA at temperatures 10–26°C are shown in Figures 2(a)–(e). These can be curve-fitted by a model proposed by Harmon et al.^{16,17} Assume that the methanol transport can be categorized as case I, case II, and anomalous absorption. The transport parameters corresponding to cases I and II are D for diffusivity and v for velocity, respectively. Letting the methanol on the surface be homogeneous and maintain the same at all times and initially no methanol be inside the PMMA, the weight gain M_t can be written as¹⁶:

$$\frac{M_t}{M_\infty} = 1 - 2 \sum_{n=1}^{\infty} \frac{\lambda_n^2 [1 - 2 \cos \lambda_n e^{-v l / 2 D}]}{\beta_n^4 \left[1 - \frac{2 D}{v l} \cos^2 \lambda_n \right]} e^{-\beta_n^2 D t / l^2}, \quad (1)$$

where

$$\lambda_n = \frac{v l}{2 D} \tan \lambda_n, \quad (2)$$

$$\beta_n^2 = \frac{v^2 l^2}{4 D^2} + \lambda_n^2, \quad (3)$$

and $2l$ is the total length of specimen. M_∞ is the equilibrium weight gain obtained at large times. Based on eq. (1), one plots the solid lines as shown in Figure 2. It is found that the theoretical curve is in good agreement with the experimental data. For the same temperature, the weight gain at any time decreases with increasing radiation dosage. Both D and v for different dosages vs. temperature are plotted in Figures 3(a) and (b), respectively. For each dosage, both D and v are satisfied with the Arrhenius equation; their activation energies are listed in Table I. It can be seen that the activation energy decreases with increasing radiation dosage. This implies that gamma irradiation enhances methanol transport in PMMA. Furthermore, one infers that methanol transport in PMMA increases with decreasing molecular weight of PMMA. In addition, for the virgin PMMA both activation energies of D and v at temperatures of 10–26°C are also higher than activation energies of D (=30.2 kcal/mol) and v (=14.4 kcal/mol) at temperatures of 40–60°C reported by Lin et al.,¹⁸ respectively.

Transmittance

When PMMA was exposed to the small dose of high-energy radiation, it became visibly discolored.¹⁹ The effect of high-energy radiation on coloration has been attributed to the production of conjugated double bonds or trapped free radicals. The transmittance as a function of wavelength for different dosages is illustrated in Figure 4(a). Note that the transmittance of virgin PMMA is 0.905. It is found that for the same wavelength, ranging from 350–800 nm, the transmittance decreases with increasing radiation dosage. When PMMA is subject to gamma irradiation in the range of 10–30 MR, the transmittance exists a local minimum (or peak) at the wavelength 405 nm. Thus, the variation of transmittance I with radiation dosage ϕ for the wavelength 405 nm is shown in Figure 4(b). This curve can be fitted with an equation as:

Table I Effect of Gamma Ray on Methanol Transport in PMMA

ϕ (MR)	0	10.4	20.8	29.7	39.6	49.5
E_D (kcal/mol)	49.8	47.8	47.5	41.2	35.6	28.3
E_v (kcal/mol)	23.3	23.3	21.1	20.0	17.7	13.1

E_D and E_v are the activation energies of D and v , respectively. ϕ is the gamma ray dose.

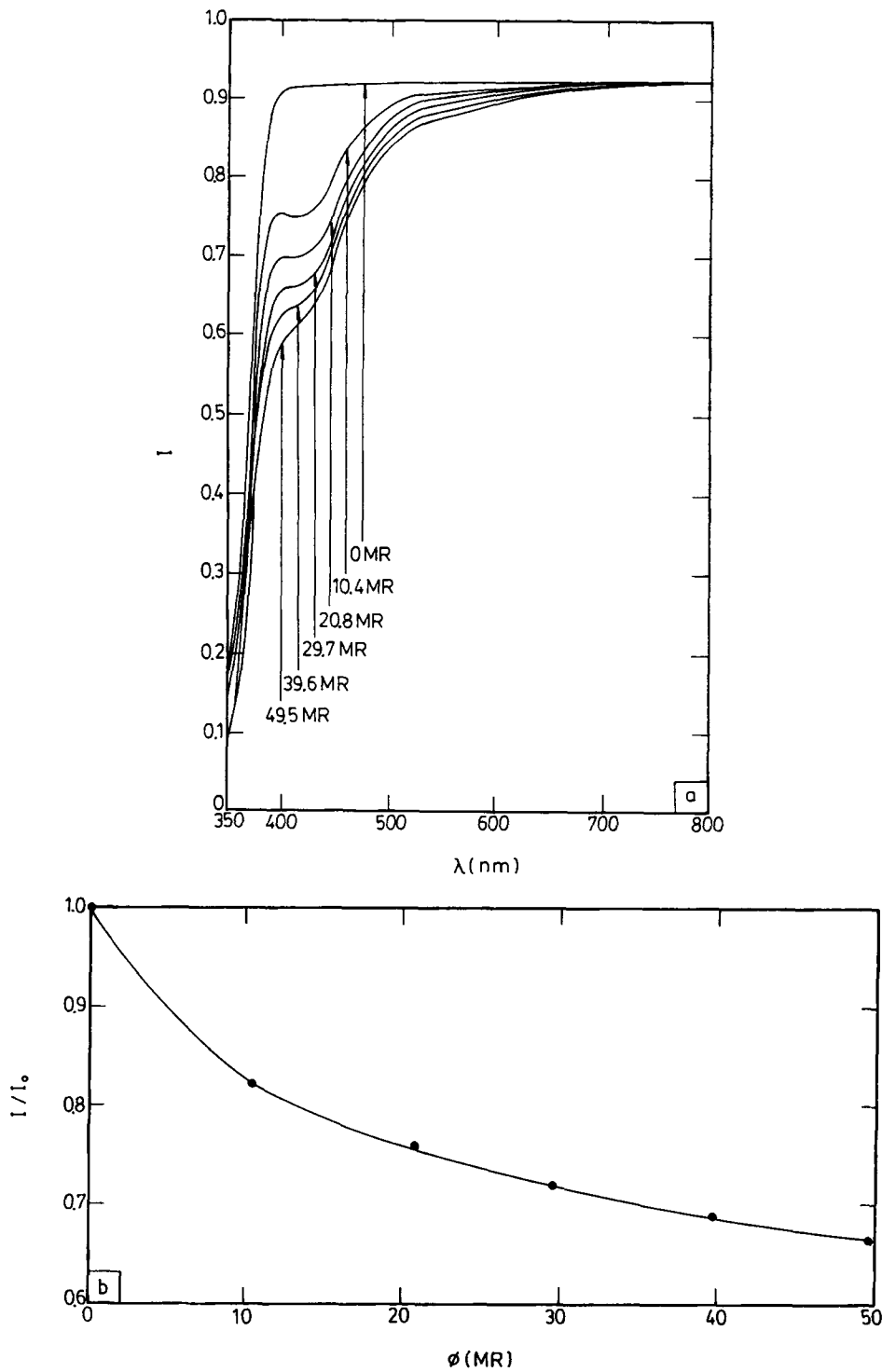


Figure 4 (a), transmittance of irradiated PMMA as a function of wavelength; (b), transmittance as a function of gamma ray dose where the wavelength is 405 nm.

$$I = I_0 \exp(-0.06\phi^{1/2}), \quad (4)$$

where I_0 , the transmittance of virgin PMMA, is equal to 0.905.

On the other hand, when the irradiated PMMA is immersed into the methanol bath at 26°C, the yellow color fades out gradually, i.e., the transmittance increases with time of exposure to methanol.

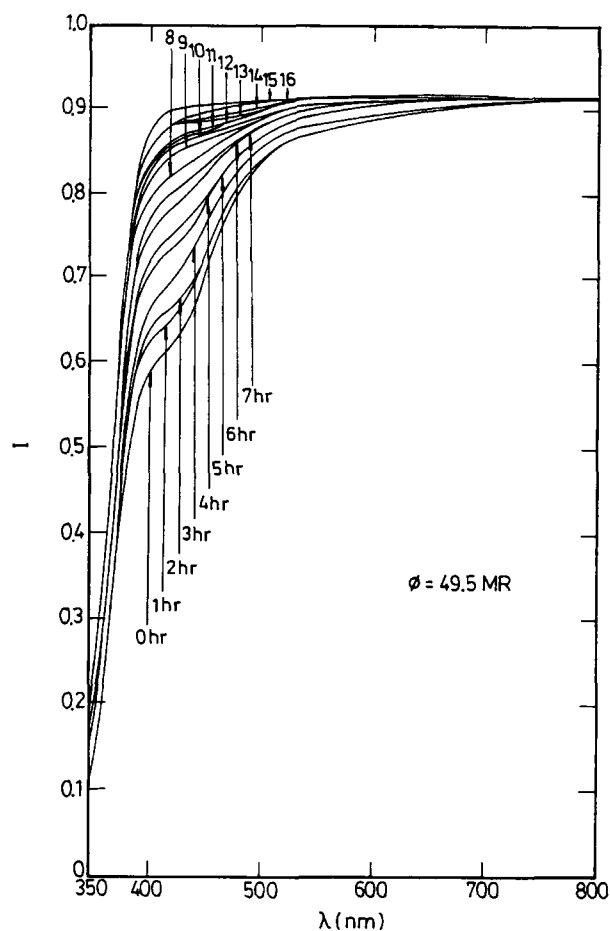


Figure 5 Transmittance of irradiated PMMA for different times of exposure to methanol as a function of wavelength. Here the gamma ray dose is 49.5 MR.

The typical transmittance of irradiated PMMA as a function of wavelength for different times of exposure to methanol is shown in Figure 5, where the gamma ray dosage is 49.5 MR. By comparing Figures 4 (a) and 5, we find that after exposure to methanol for a long time the transmittance of irradiated PMMA almost recovers to its original value. Furthermore, the transmittance as a function of time of exposure to methanol for different radiation dosages is shown in Figure 6. Two points are noteworthy to mention. First, the rate of transmittance recovery increases with increasing dosage. Second, all curves shown in Figure 6 intercept at time approximately 7 h. By comparing Figures 2 (e) and 6, one finds that the intercepted points can be fitted by the following equation:

$$\begin{aligned} [I(\phi, 7 \text{ h}) - I(\phi, 0)]/I(\phi, \infty) \\ = 0.36 M(\phi, 7 \text{ h})/M(\phi, \infty), \quad (5) \end{aligned}$$

where I and M are transmittance of irradiated PMMA and methanol content, respectively. This implies that the recovery of transmittance is proportional to the methanol content in the irradiated PMMA. Finally, after methanol desorption, the color of irradiated PMMA will recover.

Penetrant Front

After the desired amount of methanol is transported into the irradiated PMMA at temperatures of 40–

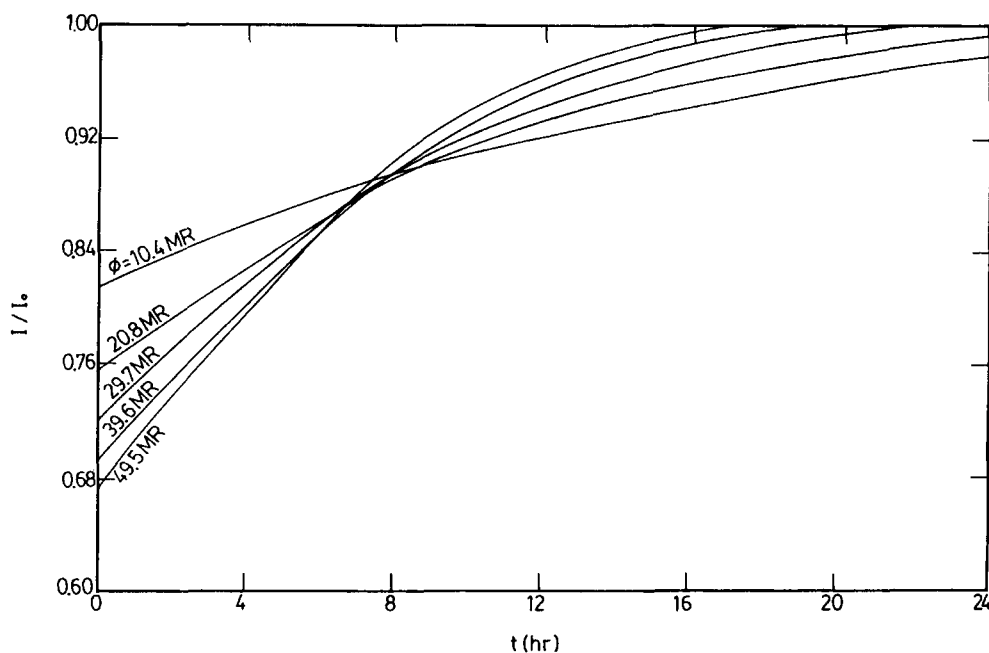


Figure 6 Transmittance of irradiated PMMA as a function of exposure time. Here the wavelength is 405 nm.

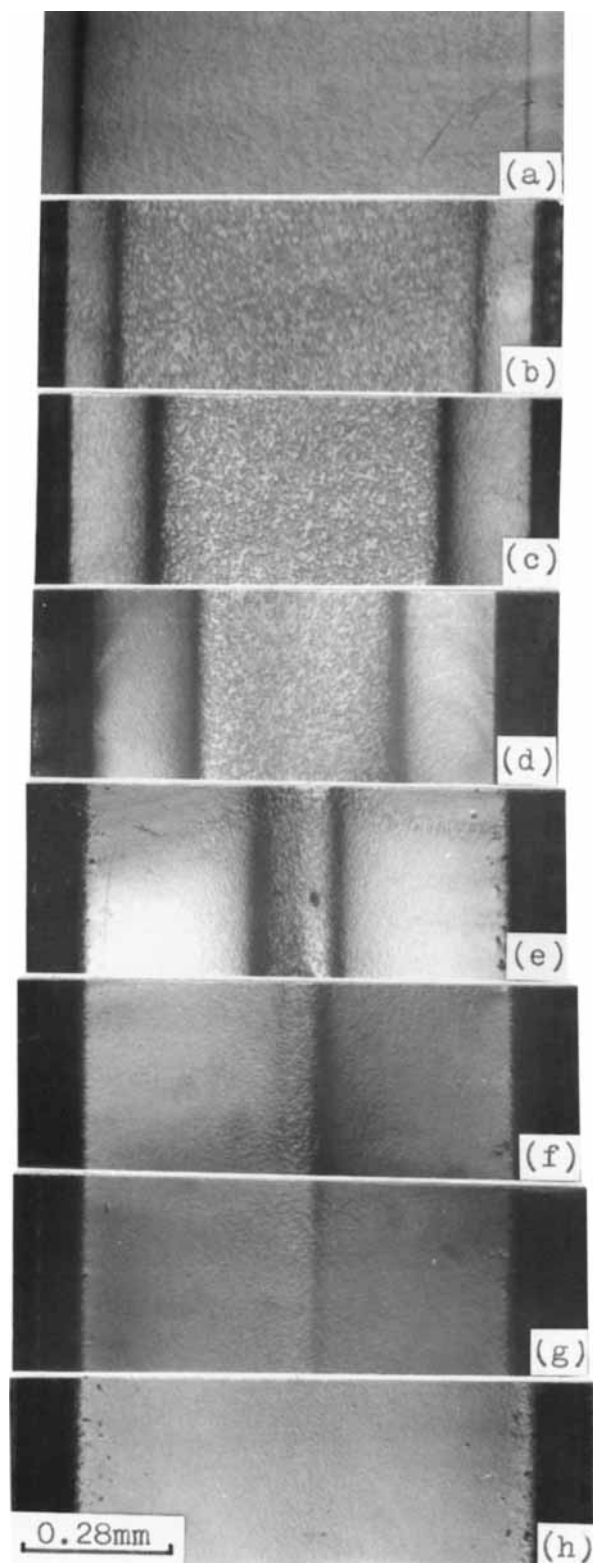


Figure 7 Sequence of photographs of PMMA subject to gamma ray dose 10.4 MR with different exposure times. (a), 15 min; (b), 35 min; (c), 45 min; (d), 60 min; (e), 90 min; (f), 110 min; (g), 140 min; (h), 160 min at 45°C was taken at temperature cooled to 26°C; (i), many cracks

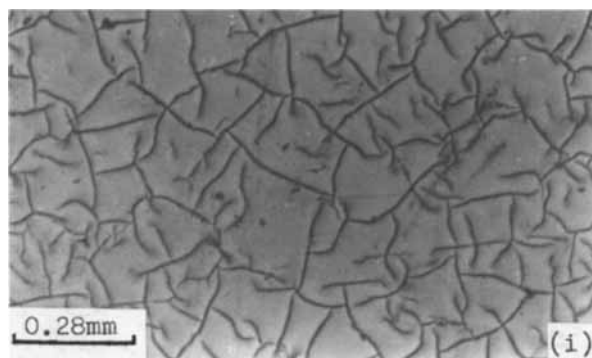


Figure 7 (Continued)

55°C, the specimen was removed from the thermostatted water bath into the air. The surfaces were blotted free of surplus methanol and the specimen was quickly photographed using a Leitz Metallux 3 optical microscope. For example, a sequence of photographs of PMMA with 10.4 MR for different times of exposure to methanol at 45°C is shown in Figures 7(a)–(h). It can be seen from Figure 7(a) that there exists a sharp boundary to separate the outer region (solvent-affected zone) from the inner region. This sharp boundary moves from surface to center as time increases, as shown in Figures 7(a)–(h). Since the introduction of methanol in the irradiated PMMA reduces the glass transition temperature of PMMA and the methanol is more rich in the outer region than in the inner region, the effective glass transition temperature of irradiated PMMA is lower in the outer region than in the inner region. This phenomenon was also observed by Thomas and Windle,²⁰ who took the photograph of the virgin PMMA specimen swollen in methanol and by Kwei and Zupko,²¹ who took the picture of the glassy polymer immersed in solvent bath. Figures 7(b)–(g) show that in addition to the regions shown in Figure 7(a) the black areas appear near the surfaces. The black area does possibly arise from the crack nucleation. Figure 7(i) shows the direct evidence of cracks appearing on the surfaces. Note that no black area was observed in the virgin PMMA treated with methanol. It is found that the inner regions (no solvent-affected zone) decrease with the increasing time of exposure to methanol. Figure 7(h) shows that methanol-affected zones appear only when exposure time is long enough, i.e., two outer solvent-affected zones meet at center. The positions of boundary between the regions with and without methanol effect at different temperatures are shown in Figures 8(a)–(e), where

appear on the surface of PMMA subject to gamma ray dose 39.6 MR with exposure time 10 min at 55°C.

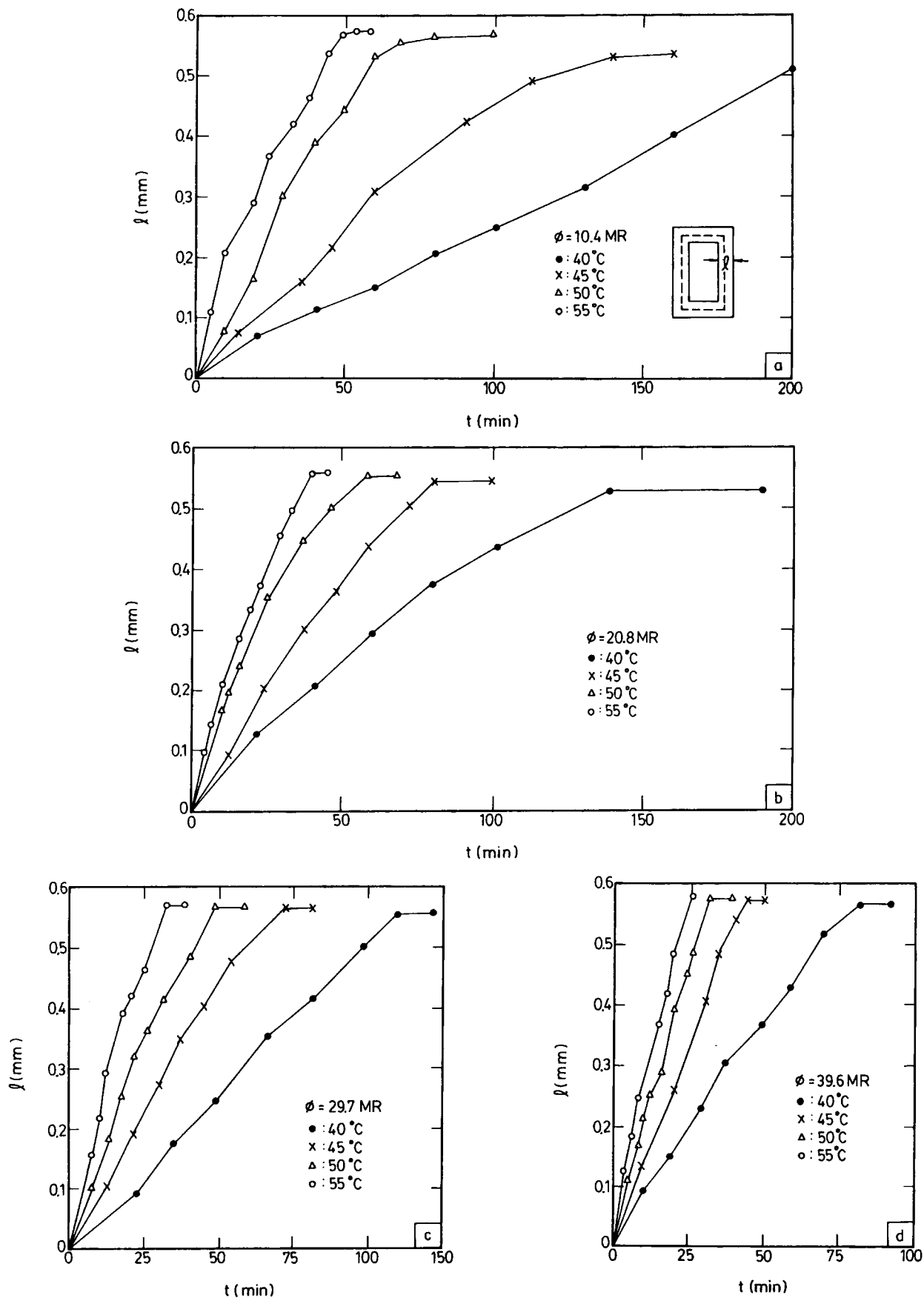


Figure 8 Distance l between sharp front and surface as a function of time of exposure to methanol at different temperatures. (a), 10.4 MR; (b), 20.8 MR; (c), 29.7 MR; (d), 39.6 MR; (e), 49.5 MR. The broken line in the inset represents the original size of the specimen.

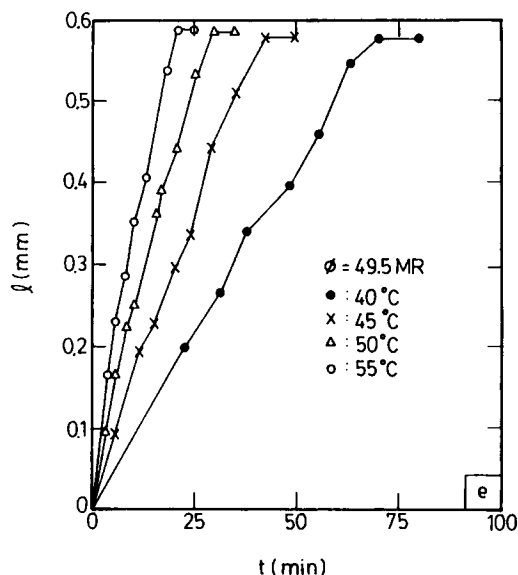


Figure 8 (continued from the previous page)

l is the distance from the surface to the boundary. The distance increases linearly with exposure time and then bends slowly until it levels off, i.e., both solvent-affected zones meet each other. The rate of boundary movement in the linear region related to gamma ray dose and operating temperature is listed in Table II. It is found that the speed of boundary movement increases with the dosage and temperature. By comparing Figure 1 and Table II, one infers that the rate of boundary movement increases with decreasing molecular weight of PMMA. In addition, the weight gain still increases slowly with exposure time after the boundary disappears.

SUMMARY AND CONCLUSIONS

The effect of methanol transport on the optical property of irradiated PMMA has been investigated. The weight gain of methanol in PMMA increases with gamma ray dosage and temperature. Both D and v for cases I and II are satisfied with the Arrhenius equation, and their activation energies increase with decreasing gamma ray dosage. It implies that gamma irradiation enhances the methanol transport in PMMA. For the same wavelength in the range 350–800 nm, the transmittance increases with decreasing radiation dosage. When irradiated PMMA is immersed into the methanol bath, the yellow color bleaches out gradually. Furthermore,

Table II Rate of Boundary Movement in the Linear Region as a Function of Gamma Ray Dose and Temperature

Temp. (°C)	ϕ (MR)					
	0	10.4	20.8	29.7	39.6	49.5
40	2.2	2.6	4.7	5.0	7.5	9.0
45	3.4	5.3	7.3	8.6	13.7	15.0
50	6.4	10.0	14.0	14.7	18.5	23.3
55	9.6	14.4	18.7	25.0	31.0	35.0

The unit of rate of boundary movement is $\mu\text{m}/\text{min}$.

the recovery of transmittance of irradiated PMMA is proportional to the methanol content in the irradiated PMMA. After the irradiated PMMA treated with methanol was removed from a thermostatted water bath into the air, a sharp boundary to separate the outer region (solvent-affected zone) from the inner region was found. The rate of boundary movement at the small exposure times increases with the dosage and temperature. At the intermediate times, the black area near the surface was observed. At the large times, the sharp boundary disappears.

This work was supported by National Science Council, Taiwan, Republic of China.

REFERENCES

1. R. Simha, *Trans. N.Y. Acad. Sci.*, **14**, 151 (1952).
2. A. A. Miller, E. J. Lawton, and J. S. Balwit, *J. Polym. Sci.*, **XIV**, 503 (1954).
3. E. J. Lawton, H. M. Bueche, and J. S. Balwit, *Nature*, **172**, 76 (1953).
4. L. A. Wall and D. W. Brown, *J. Phys. Chem.*, **61**, 129 (1957).
5. A. C. Ouano, D. E. Johnson, B. Dawson, and L. A. Pederson, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 701 (1976).
6. G. J. Pratt, *J. Mater. Sci.*, **10**, 809 (1975).
7. P. R. Shultz, P. I. Roth, and G. B. Rathman, *J. Polym. Sci.*, **22**, 495 (1956).
8. H. N. Subrahmanyam and S. V. Subramanyam, *Polymer*, **28**, 1331 (1987).
9. W. Knappe and O. Yamamoto, *Kolloid Z.*, **240**, 775 (1970).
10. A. J. Todd, *J. Polym. Sci.*, **42**, 223 (1969).

11. C. David, D. Fuld, and G. Geuskens, *Makromol. Chem.*, **139**, 269 (1970).
12. S. I. Ohnishi and I. Nitta, *J. Polym. Sci.*, **XXXVIII**, 451 (1959).
13. R. P. Kusy and M. J. Katz, *J. Mater. Sci.*, **11**, 1475 (1976).
14. D. T. Turner, *Polymer*, **28**, 293 (1987).
15. Kalachandra and D. T. Turner, *Polymer*, **28**, 1749 (1987).
16. J. P. Harmon, S. Lee, and J. C. M. Li, *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 3215 (1987).
17. J. P. Harmon, S. Lee, and J. C. M. Li, *Polymer*, **29**, 1221 (1988).
18. C. B. Lin, S. Lee, and K. S. Liu, *Polym. Engng. Sci.*, **30**, 1399 (1990).
19. P. Charlesby, P. Alexander, and M. Ross, *Proc. Roy. Soc. (London)*, **A223**, 392 (1954).
20. N. L. Thomas and A. H. Windle, *Polymer*, **19**, 255 (1978).
21. T. K. Kwei and H. M. Zupko, *J. Polym. Sci.*, **A-2**, **7**, 867 (1969).

Received March 20, 1991

Accepted July 11, 1991