

Light Scattering Study on the Structure of Pure Poly(methyl methacrylate)

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(Received March 16, 1983)

ABSTRACT: The polarized and depolarized components of light scattering by pure poly(methyl methacrylate) (PMMA) were measured as a function of temperature above and below T_g . The PMMA sample used was prepared by a very careful procedure in which the evaporable monomer, initiator, and chain transfer agent were distilled in a closed vacuum system and *in-situ* polymerization was carried out above T_g . The measured V_v^{iso} intensities were favorably compared with the values calculated from thermal density fluctuation in the temperature range from 20 to 140°C. The measured intrinsic H_v intensity was fairly close to the value calculated assuming a randomly oriented anisotropic liquid for PMMA. Our experiment showed no evidence for an ordered structure in pure PMMA glass, as is found in pure polystyrene glass.

KEY WORDS Light Scattering / Poly(methyl methacrylate) / Fluctuation / Local Structure / Amorphous Polymer /

Poly(methyl methacrylate) (PMMA) and polystyrene (PS), typical amorphous polymers, are quite transparent in the visible and near infrared region. These polymers have been used as plastic optical fibers (POFs). However, commercial PMMA core POFs have large losses of at least about $7.0 \times 10^{-4} \text{ cm}^{-1}$ (650 nm).¹ Recently, we obtained by a modified vacuum distillation procedure low-loss POFs which had attenuation losses of $2.05 \times 10^{-4} \text{ cm}^{-1}$ (522 and 570 nm) for a PMMA core fiber² and $2.62 \times 10^{-4} \text{ cm}^{-1}$ (672 nm) for a PS core fiber.³ This procedure allowed PMMA and PS fibers to be highly purified both optically and chemically. To clarify the cause for optical loss and the theoretical attenuation limits for PMMA and PS, it is very important to examine these polymers by light scattering.

The local structure of polymer molecules in the amorphous state is a current subject of considerable interest and controversy.⁴⁻⁷ A number of light and X-ray scattering experiments have been reported for PMMA,⁸⁻¹⁶ PS,¹⁵⁻²¹ and other amorphous polymers.²²⁻²⁴

Excess light scattering intensities are invariably

found in PMMA glasses, and have been attributed to the existence of semi-crystalline regions, internal frozen strain, low molecular weight species, and micro-inhomogeneities or dust. Recently, from a light scattering study on PMMA glasses prepared by MMA monomer distillation, Judd and Crist⁸ concluded that PMMA has an intrinsic structure of about 800 Å dimensions. On the other hand, Claiborne and Crist²⁰ studied light scattering from PS glasses prepared by monomer distillation, and concluded that no particular structure other than that expected for supercooled amorphous polymers exists.

We consider this discrepancy between PMMA and PS glasses to occur from the difference in conditions used for sample preparation. The PMMA sample was prepared by polymerization below T_g and its viscosity-average molecular weight was very high, 2.6×10^6 ,⁸ while the PS sample was prepared by polymerization above T_g and its weight-average molecular weight was relatively low, about 4×10^5 .²⁰ Since, as is well known, free radical bulk polymerization causes the auto-acceleration effect, it may lead to micro-inhomogeneities in the

sample by the formation of crosslinked or branched species. This effect is pronounced in the polymerization of MMA below T_g . Probably, microinhomogeneities induced by the auto-acceleration effect were present in the PMMA glasses prepared by Judd and Crist.

In this paper, we describe a light scattering study performed to determine whether an ordered structure exists in the glassy and liquid state of PMMA. For this purpose, we made special efforts to prepare extremely pure PMMA samples.

EXPERIMENTAL

Methyl methacrylate (MMA) was prepared by the following process. First, polymerization inhibitors were eliminated by rinsing with alkali. The residual alkali was then removed by washing with pure water until the pH of the system became neutral. After being dried by the addition of Na_2SO_4 and CaH_2 , the monomer was carefully distilled under reduced pressure in a stream of Ar gas, and a center fraction was collected (bp 65.5–66.5°C/250 mmHg).

Di-*tert*-butylperoxide (DBPO) chosen as the initiator was carefully distilled under reduced pressure (bp 46.5–47.8°C/80 mmHg). *N*-butylmercaptan (NBM) was used as a chain transfer agent to depress auto-acceleration effects (bp 97.3–98.1°C/760 mmHg).

MMA containing 1.0×10^{-2} M DBPO and 4.0×10^{-2} M NBM was poured into ampoule A in the apparatus shown in Figure 1 and degassed under 0.1 mmHg, taking care to prevent dust and oxygen from entering the ampoule. Then, part C was sealed. Ampoules A and B were maintained at

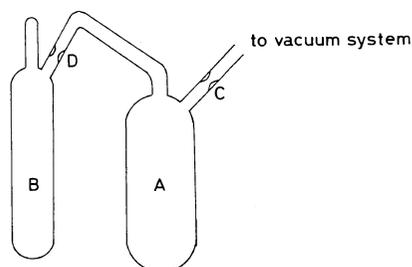


Figure 1. Apparatus used in the vacuum distillation sample preparation.

30 and 0°C, respectively. Ampoule B, with optically polished internal and external walls, was 20 mm in diameter and 200 mm in length. After distillation, the entire assembly was shaken and the MMA containing the additives in ampoule B was transferred to ampoule A, and ampoule B was washed. After this process was repeated several times, no glittering due to optical impurities, such as dust and large particles, could be detected at all when the He-Ne laser beam was passed through ampoule B. Finally, ampoule B containing pure MMA was sealed at part D, and the polymerization of MMA was allowed to proceed for 48 h at 120°C, for 12 h at 140°C, and then for 2 h at 160°C. From GPC measurement, the weight-average molecular weight of the polymer sample was found to be 4.3×10^4 and the polydispersity index, $M_w/M_n = 1.7$.

A block diagram of our light scattering apparatus is shown in Figure 2. A 0.95 mW He-Ne laser (Spectra Physics Co., Model 155) was used as the light source. This low power laser beam prevented the sample from local heating due to the 6th order C-H stretching vibration of PMMA (*ca.* 1.4×10^{-4}

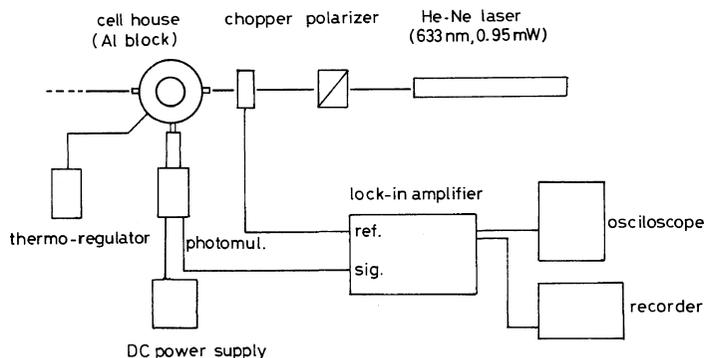


Figure 2. Diagram of the scattering measurement system.

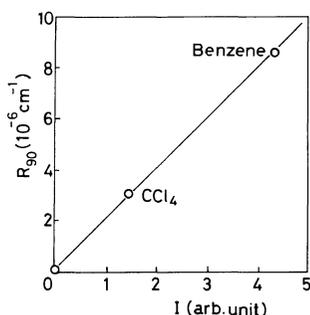


Figure 3. Relation between the Rayleigh ratio for the standard samples and scattered light intensity.

$\text{cm}^{-1.2}$). The scattered light at an angle of 90° was detected by a photomultiplier tube (Hamamatsu TV Co., Model R189). The cell housing for the PMMA sample was held in a temperature-regulated aluminum block. The sample was heated or cooled at a rate of $0.1^\circ\text{C}/\text{min}$ in the cell housing, and was sufficiently annealed at desired temperatures. The frequency of the chopper used as an external trigger was 55 Hz. The time constant of the lock-in amplifier (NF Co., Model LI 572A) was 1.0 s and the signal drift of scattered light remained within $\pm 1\%$. No analyser was used since this arrangement was more effective for eliminating stray light. A linear relationship was obtained between the Rayleigh ratio, R_{90} , and the scattered light intensity for the standard scattering samples,²⁷ as shown in Figure 3. Close agreement was obtained between the measured and published depolarization factors, ρ_u , for either standard sample; the measured ρ_u was 0.412 for benzene and 0.049 for carbon tetrachloride at $\lambda_0 = 633 \text{ nm}$ (benzene: $\rho_u = 0.42$ at $\lambda_0 = 546 \text{ nm}$; carbon tetrachloride: $\rho_u = 0.042$ at $\lambda_0 = 546 \text{ nm}$).²⁷ These preliminary results show that the polarized and depolarized components of scattered light can be well separated by the present simple measuring system.

Refractive indices of PMMA for the Na-D line, n_D , were measured using a thermostated Abbe refractometer (Atago Co., Model 2 with Haake Co., Model FE2).

RESULTS AND DISCUSSION

To determine the density fluctuation and anisotropy fluctuation, polarized (H_v and H_h) and depolarized (V_v and V_h) intensities were calculated

from the following equations on the assumption that $H_v = V_h = H_h$ for a randomly oriented spheroid:^{25,26}

$$R_{90} = \frac{V_v + V_h + H_v + H_h}{2} = \frac{V_v + 3H_v}{2} \quad (1)$$

$$\rho_u = \frac{V_h + H_h}{V_v + H_v} = \frac{2H_v}{V_v + H_v} \quad (2)$$

$$V_v = V_v^{\text{iso}} + \frac{4}{3} H_v = R_{90} \frac{2 - \rho_u}{1 + \rho_u} \quad (3)$$

$$V_v^{\text{iso}} = R_{90} \frac{2 - \frac{7}{3} \rho_u}{1 + \rho_u} \quad (4)$$

$$H_v = R_{90} \frac{\rho_u}{1 + \rho_u} \quad (5)$$

where V_v and H_v are the vertical and horizontal components of the scattered light intensity for vertically polarized incident light, V_h and H_h , the corresponding quantities for horizontally polarized incident light, and V_v^{iso} , the isotropic part of the V_v component. The value of V_v , V_v^{iso} , and H_v can be evaluated by substituting measured R_{90} and ρ_u into eq 3–5.

The V_v^{iso} and H_v of light scattered by a structureless liquid can be calculated from the expressions^{26,28}:

$$V_v^{\text{iso}} = \frac{\pi^2}{9\lambda_0^4} ((n^2 - 1)^2 (n^2 + 2)^2 kT\beta) \quad (6)$$

$$H_v = \frac{16\pi^2}{135\lambda_0^4} (n^2 + 2)^2 N_0 \gamma^2 \quad (7)$$

Equation 6 gives the polarized Rayleigh ratio resulting from thermal density fluctuation as a function of wavelength λ_0 of incident light in vacuum, the average refractive index n , the Boltzmann constant k , the absolute temperature T of liquid or glass, and the isothermal compressibility β at T_g . Equation 7 gives the depolarized scattering arising from the mean-square polarizability anisotropy γ^2 of scattering centers; for polymers, N_0 is the number of monomer repeat units.⁹

The measured values of V_v and H_v for pure PMMA are shown as functions of temperature in Figure 4. The V_v intensity decreases smoothly with decreasing temperature from 160 to 90°C near T_g of PMMA (105°C), and undergoes a small amount of

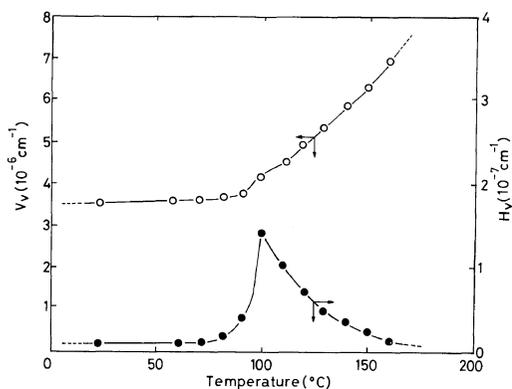


Figure 4. Temperature dependence of V_v and H_v components for pure PMMA ($\lambda_0 = 633$ nm).

change from 90 to 20°C. On the other hand, the H_v intensity shows a maximum near T_g . The variations in V_v and H_v with temperature were quite reversible above T_g when the temperature was changed slowly.

The temperature dependence of thermal and anisotropy fluctuations in PMMA glass has been studied using light scattering and other techniques. Patterson,¹⁰ studying polarized and depolarized light scattering from a cast and polished block of PMMA, found that the V_v intensity decreased smoothly with decreasing temperature to T_g but virtually remained invariable below T_g , and that the H_v intensity was almost constant both above and below T_g . However, he reported no absolute values of V_v and H_v . Dettenmaier and Fischer,⁹ who studied the V_v component for a commercial block of PMMA, found that the V_v intensity exhibited a maximum just below T_g and a minimum just above T_g . Ruland¹⁶ studied density fluctuation in commercial PMMA and PS in the range from 0 to 400 K using SAXS, and found that the fluctuation *vs.* T curves of these polymers showed breaks at T_g . Above T_g , the fluctuation intensity varied with T , following the relationship valid for a system in thermodynamic equilibrium, while below T_g , the fluctuation intensity *vs.* T curve approached a non-zero value at 0 K with decreasing T .

The trend of the V_v - T curve obtained in the present experiment resembles the results reported by Patterson¹⁰ and Ruland.¹⁶ However, our H_v - T curve was not comparable to the results reported by Patterson.¹⁰ Our results suggest that the strained

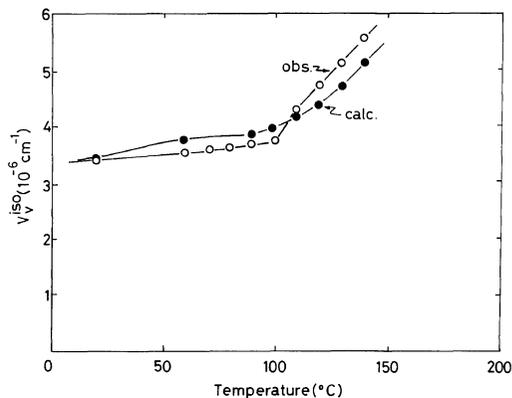


Figure 5. Temperature dependence of observed and calculated V_v^{iso} components for pure PMMA ($\lambda_0 = 633$ nm).

polymer adheres to the ampoule glass wall in the glass-rubber transition region or that an anisotropic structure is produced and disappears at the temperature near T_g . The causes for such phenomena may be the relatively low molecular weight of our sample, 4×10^4 .

The observed and calculated V_v^{iso} values above and below T_g are shown in Figure 5. In the temperature range below T_g , the V_v^{iso} was calculated by substituting the n_D values at measured temperatures and the reported β value²⁹ at 120°C into eq 6, while in the temperature range above T_g , the n_D , T , and β ²⁹ values at measured temperatures were substituted. The observed V_v^{iso} values are in good agreement with those calculated throughout the entire temperature range, indicating that PMMA glass is in a frozen thermal density fluctuation state near T_g . Ruland¹⁶ and Fischer *et al.*¹¹ determined the temperature dependence of density fluctuation for PMMA by SAXS and found that PMMA was in the thermodynamic non-equilibrium state in a temperature range from T_g down to about $T_g - 50$. The $V_v^{\text{iso}}-T$ curve obtained in the present experiment is consistent with their finding.

Our H_v value of 8.5×10^{-9} cm⁻¹ at $\lambda_0 = 633$ nm does not differ greatly from $(0.02-1.2) \times 10^{-6}$ cm⁻¹ at $\lambda_0 = 633$ nm, predicted with the published value of γ^2 .⁸ However, it differs by a factor of the order of 10^{-2} from previous results: Dettenmaier,⁹ $H_v = 2.8 \times 10^{-7}$ cm⁻¹ at $\lambda_0 = 633$ nm and Judd and Crist,⁸ $H_v = 4.1 \times 10^{-7}$ cm⁻¹ at $\lambda_0 = 578$ nm. This discrepancy may be due to the difference in chain

transfer agent used in the preparation of the samples. By conducting the chain transfer reaction at a temperature above T_g , the generation of microinhomogeneities due to the auto-acceleration effect and increase in polymerization rate may be suppressed. With the value of H_v and the number of monomer units per cm^3 inserted in eq 7, the anisotropy value γ_0^2 for a monomer unit can be obtained. If a randomly oriented anisotropic liquid is assumed for PMMA glass, we obtain $1.6 \times 10^{-49} \text{ cm}^6$ for γ_0^2 . This is only 8 times larger than the value evaluated by Fischer *et al.*¹¹ from the stress optical coefficient, suggesting that no ordered anisotropic structure induced by collisions, orientational correlation, or frozen strains exists in well-annealed pure PMMA glass.

CONCLUSION

Our light scattering data for PMMA glass prepared from a pure monomer and additives at a temperature above T_g were consistent with the scattering behavior expected for supercooled liquid. From the temperature dependence of the V_v^{iso} component, it was found that light scattering from PMMA in the 20 to 160°C range can be adequately attributed to thermal density fluctuation. Thus, PMMA glass near T_g is in a state at which thermal density fluctuation is frozen. Further, the temperature dependence of the H_v component for pure PMMA showed a characteristic feature such that H_v attains a maximum at T_g . This excess H_v intensity may be attributed to either the strained polymer molecules adhering to the ampoule glass wall or the generation of an anisotropic structure. The value of γ_0^2 calculated from the intrinsic H_v intensity, assuming a randomly oriented anisotropic liquid for PMMA, was only 8 times as large as the value from the stress optical coefficient. In summary, our light scattering experiment gave no evidence for the presence of an ordered structure in pure PMMA glass and liquid, as in pure PS glass. We may note that this conclusion was obtained with a very carefully prepared polymer sample.

Acknowledgements. General assistance by Yuzo Katayama, Shigeo Nara, and Toshiro Hirai is gratefully acknowledged. The assistance of Takeshi Yamada in measuring PMMA refractive indices is appreciated. This scattering experiment was ini-

tiated at the suggestion of Toshiro Hirai.

REFERENCES

1. H. M. Schleiniz, *Int. Wire and Cable Symp.*, **25**, 352 (1977).
2. T. Kaino, M. Fujiki, S. Oikawa, and S. Nara, *Appl. Opt.*, **20**, 2886 (1981).
3. T. Kaino, M. Fujiki, and S. Nara, *J. Appl. Phys.*, **52**, 7061 (1981).
4. P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).
5. W. Pechhold, *Kolloid Z. Z. Polym.*, **228**, 1(1968).
6. C. C. Kampf, J. Hofmann, and H. Kramer, *Ber. Bunsenges.*, **74**, 851 (1970).
7. G. S. Y. Yeh, *J. Macromol. Sci., Phys.*, **B6**, 465 (1972).
8. R. E. Judd and B. Crist, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 717 (1980).
9. M. Dettenmaier and E. W. Fischer, *Kolloid Z. Z. Polym.*, **251**, 922 (1973).
10. G. D. Patterson, *J. Macromol. Sci., Phys.*, **B12**, 61 (1976).
11. E. W. Fischer, J. H. Wendorff, M. Dettenmaier, G. Lieser, and I. Voigt-Martin, *J. Macromol. Sci., Phys.*, **B12**, 41 (1976).
12. A. B. Romberger, D. P. Eastman, and J. L. Hunt, *J. Chem. Phys.*, **51**, 3723 (1969).
13. E. A. Friedman, A. J. Ritger, and R. D. Andrews, *J. Appl. Phys.*, **40**, 4243 (1969).
14. E. Kato, *J. Chem. Phys.*, **76**, 2763 (1982).
15. M. Dettenmaier and E. W. Fischer, *Makromol. Chem.*, **177**, 1185 (1976).
16. W. Ruland, *Pure Appl. Chem.*, **49**, 905 (1977).
17. R. W. Coakley, R. S. Mitchell, J. R. Stevens, and J. L. Hunt, *J. Appl. Phys.*, **47**, 4271 (1976).
18. H. Lee, A. M. Jamieson, and R. Simha, *Coll. Polym. Sci.*, **258**, 545 (1980).
19. G. R. Alms, G. D. Patterson, and J. R. Stevens, *J. Chem. Phys.*, **70**, 2145 (1979).
20. C. Claiborne and B. Crist, *Coll. Polym. Sci.*, **257**, 457 (1979).
21. R. W. Coakley, R. S. Mitchell, J. L. Hunt, and J. R. Stevens, *J. Macromol. Sci., Phys.*, **B12**, 511 (1976).
22. J. V. Champion and P. Liddle, *Polymer*, **21**, 1247 (1980).
23. J. R. Stevens, D. A. Jackson, and J. V. Champion, *Mol. Phys.*, **29**, 1893 (1975).
24. J. E. Guillet, R. S. Mitchell, E. Dan, and J. P. Valleau, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 625 (1972).
25. M. B. Huglin, "Light Scattering from Polymer Solution," Academic Press, New York, N. Y., 1972.
26. M. Kerker, "The Scattering of Light and Other Electromagnetic Radiation," Academic Press, New York, N. Y., 1972.
27. D. J. Coumou, E. L. Mackor, and J. Hijmans, *Trans.*

- Faraday Soc.*, **60**, 1539 (1964).
28. A. Einstein, *Ann. Phys.*, **33**, 1275 (1910).
29. K. H. Hellwege, W. Knappe, and P. Lehman, *Kolloid Z. Z. Polym.*, **183**, 110 (1962).