Dynamic Viscoelastic Measurements of Photosensitive Polymers

KOICHIRO WATANABE, TAKESHI AMARI, and YASUFUMI OTSUBO,
Department of Image Science and Technology, Faculty of Engineering,
Chiba University, 1-33, Yayoi-cho, Chiba-shi, 260 Japan

Synopsis

A new type of rheometer for measuring the dynamic viscoelastic properties of photosensitive polymers was developed. When the photosensitive polymer is exposed to ultraviolet (UV) irradiation, the dynamic modulus and dynamic viscosity increase with time due to network polymerization. Since the curing is completed within a few seconds, the apparatus is designed to follow the rapid changes in rheological properties. The most significant advantages of this apparatus are as follows: (1) The required amount of sample is extremely small (about 0.01 mg). (2) Although the measurements are carried out with liquid polymer, a cell for sample is not necessary. (3) Since the sample thickness is about 10 μm, the temperature can be easily controlled. (4) By measuring the thickness before and after UV irradiation, the volume contraction of the sample can be determined. The curing behavior is measured for urethane acrylate and epoxy acrylate prepolymers, and the effect of acetophenone and benzoin which act as photoinitiators, is examined. Acetophenone ensures more efficient absorption of UV light than benzoin.

INTRODUCTION

Ultraviolet (UV) curing is of increasing interest for applications in image recording. This technique has the advantage of efficient use of energy and rapid cure rate, in contrast to other heating procedures. The photochemical processes of many organic molecules have been extensively studied, but the photochemistry related directly to printing and coating technology is still being explored. Difficulty in systematic study results from the complex manner on which the chemistry of UV curing varies depending on the pigments dispersed in the vehicle and on the substrates to be printed.[1,2] For instance, carbon black causes problems because it absorbs UV irradiation energy.[3]

A number of methods have been used to determine the rate and degree of curing for photosensitive polymers. The most frequently used parameter is gel fraction, which is determined by the weight of insoluble gel formed by network polymerization. To obtain the relation between exposure energy and gel fraction, several experiments were repeated at different exposure times for each polymer. Moreover, since the photosensitive polymer causes a dark reaction after cessation of UV irradiation, this effect should be taken into account in the analysis of data.

There are correlations between the degree of curing and physical properties such as specific volume[4] and electrical resistance.[5] Rheological behavior is also an important aspect of UV curing. In order to study the rheological properties of pigment suspensions, various rheometers are used in steady shear and oscillatory shear modes.[6–8] However, use of typical rheometers such as coaxial cyl-

Journal of Applied Polymer Science, Vol. 29, 57–66 (1984)
CCC 0021-8995/84/010057-10$04.00

inder and cone-and-plate types are not appropriate for photosensitive polymers because the sample changes from a viscous liquid to a viscoelastic solid within a few seconds. We have focused attention on the method of measuring viscoelastic behavior during such rapid processes. From the measurements of viscoelastic properties of photosensitive polymers during curing processes, we can deduce the structural changes and investigate the kinetics of processes. This paper describes an instrument designed to enable dynamic viscoelastic measurements during UV curing.

APPARATUS

The apparatus developed in this study is essentially an oscillating plate rheometer in which the sample is sheared in space between a fixed plate and an oscillating plate.[9] A schematic diagram of the system is shown in Figure 1. An extremely small amount of photosensitive polymer is placed on an adjustable table and pressed against a quartz glass. The quartz glass is attached to a duralumin frame, and the latter is horizontally held by suspension wires. A forced oscillation is applied electromagnetically by passing an alternating current through a coil in a constant radial magnetic field. The displacement of the frame is detected as a change in capacity of a small condenser consisting of a set of parallel copper plates.

The mechanical impedance of the system **Z** is defined as the ratio between the applied sinusoidal force **F** and resultant displacement **S**:

$$\mathbf{Z} = \mathbf{F}/\mathbf{S} = (G'/C - \omega^2 M + k) + i\omega\eta'/C \tag{1}$$

where G' is the dynamic modulus, η' is the dynamic viscosity, ω is the angular frequency, M is the mass of the moving components, k is the wire constant, and C is the shape factor given by h/A, where h and A are the thickness and area of the sample, respectively.

Introducing the following equations

$$m = |\mathbf{F}|/|\mathbf{S}| = \sqrt{(G'/C - \omega^2 M + k)^2 + (\omega\eta'/C)^2} \tag{2}$$

$$\tan\phi = \frac{\omega\eta'}{G' - \omega^2 CM + kC} \tag{3}$$

we have

$$G' = C(m\cos\phi + \omega^2 M - k) \tag{4}$$

$$\eta' = (mC\sin\phi)/\omega \tag{5}$$

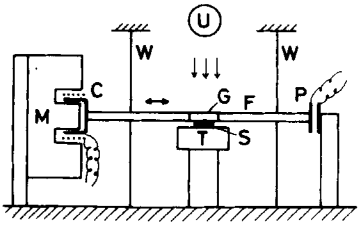

Fig. 1. Schematic diagram of apparatus: (C) driving coil; (F) frame; (G) quartz glass; (M) magnet; (P) condenser pick-up; (S) sample; (T) adjustable table; (U) UV light; (W) suspension wires.

Thus, the dynamic modulus G' and dynamic viscosity η' can be obtained by measuring the amplitude ratio m and phase angle ϕ.

Figure 2 shows a block diagram of the electrical circuit. A variable frequency oscillator supplies an alternating current to the circuit, consisting of the driving coil and a constant resistance. The voltage drop across this constant resistance is a measure of the current in the coil and is monitored with an oscilloscope. The signal from the oscillator is also sent to the phase detector. The output voltage from the displacement meter, which is a measure for the sinusoidal displacement of the frame, is directly fed into the phase detector. The phase detector is used to measure the phase angle between the driving voltage (force) and the output voltage (displacement). Both the output voltage and the phase angle are registered with a photorecorder through amplifiers. When the UV light is applied to the photosensitive polymer, the dynamic modulus and dynamic viscosity rapidly increase due to network polymerization; then the movement of the quartz glass rapidly decreases with time. Since the samples used in this study were completely cured in a few seconds, a photorecorder was used for recording such a rapid change.

CALIBRATION OF THE APPARATUS

Forced oscillation experiments without the sample in the rheometer provide the wire constant and the mass of the moving components. The resultant values are $k = 7.03 \times 10^3$ N·m^{-1}, and $M = 18.9$ g with an accuracy of about 2%.

The force applied to the frame is equal to BLI, where B is the magnetic induction in the magnet gap, L is the length of the wire in the coil, and I is the current passing through the coil. When a direct current is supplied to the coil without the sample, eq. (1) results in

$$BLI = kS \tag{6}$$

Figure 3 shows the relation between the current passing through the coil and the displacement of the frame. The displacement is measured with a traveling microscope. Since k is already known, BL can be calculated from the slope of straight line and is determined as $BL = 4.98$ N·A^{-1}.

The pickup condenser consists of two copper plates 3 cm in width and 6 cm in length. One plate is attached to the end of the moving frame, the other set

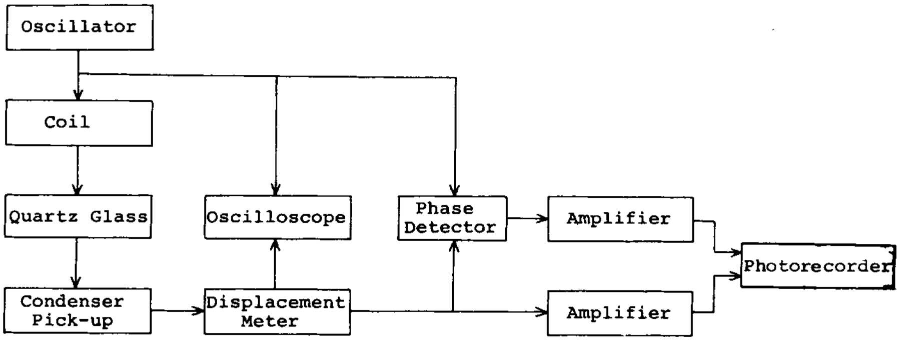

Fig. 2. Block diagram of electrical circuit.

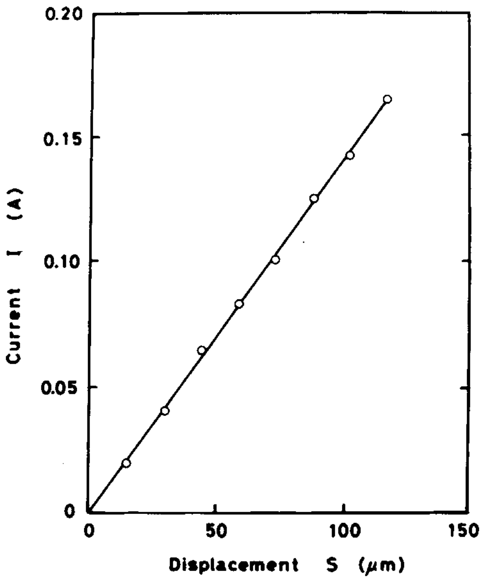

Fig. 3. Relation between the current passing through the coil and the displacement of frame.

to the stationary block. The distance between the two plates is about 0.1 cm in order to get sufficient capacity. The plates must be set parallel to each other, and we can measure the displacement within an accuracy of 0.5 μm.

Certain problems were found in calculating the dynamic modulus. Equation (4) is derived by equating the real term on the right side of eq. (1) to the force in phase with the displacement; this implies that the forces due to elastic response of sample, inertia, and elasticity of wires are in phase. Careful attention must be paid to the accurate measurement of dynamic modulus. In ordinary experiments, the measuring frequencies are less than the resonance frequency of the system. The system should be so arranged that the force due to elastic response of sample governs the behavior. However, it would be still difficult to monitor the change in dynamic modulus through the entire course of UV curing because the photosensitive polymer changes from a viscous liquid to a solid film. On the other hand, by roughly matching the characteristics of the system with that of the sample, the time dependence of dynamic viscosity can be measured. Therefore, in this study, the UV curing behavior is discussed in terms of dynamic viscosity.

DETERMINATION OF SAMPLE THICKNESS[10]

The dynamic viscosity of the prepolymer (before UV irradiation) is independent of sample thickness. However, if the sample is thick, the curing behavior under irradiation may vary in the direction perpendicular to the shearing surfaces. To avoid this inconsistency in the photochemical process, the sample has to be kept as thin as possible. In this study, the sample thickness was controlled by the use of an optical interferometer.

Figure 4 shows an optical arrangement for measurement of the sample thickness. A light beam from a monochrometer is reflected by a mirror and led

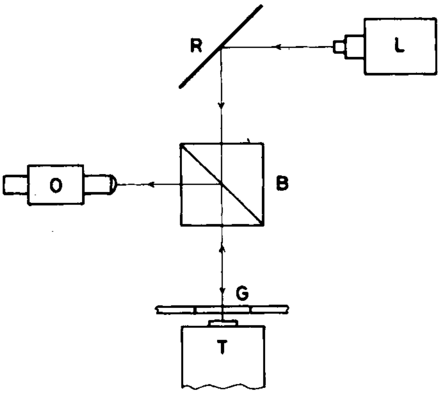

Fig. 4. Optical arrangement for measurement of sample thickness: (B) beam splitter; (G) quartz glass; (L) monochrometer; (O) microscope; (R) mirror; (T) adjustable table.

to the narrow gap between the quartz glass and sample table through a beam splitter. The principle of operation is shown in Figure 5. Assuming that the quartz glass and sample table are not exactly parallel, but incline very slightly toward each other, one can find interference fringes by a microscope. The interference fringes appear at the positions where the light reflected by the quartz glass has the reverse phase of that by the sample table, i.e.,

$$2h = n\lambda_0 \tag{7}$$

where n is an integer number and λ_0 is the wavelength. When the wavelength is gradually decreased,the fringes slowly shift. If the wavelength is so decreased that the reference fringe shifts to the position where the neighboring fringe was located at the wavelength of λ_0, the resultant wavelength λ_1 can be described by

$$2h = (n + 1)\lambda_1 \tag{8}$$

Similarly, let the wavelength be λ_m for the shift to the mth fringe; then the sample thickness is given by

$$h = \frac{m}{2}\frac{\lambda_0\lambda_m}{\lambda_0 - \lambda_m} \tag{9}$$

In the experiments, three or four fringes were observed in the field of 5 mm × 6 mm at a wavelength of 500 nm. Thus the difference in the distance was about 0.75 μm. As the sample was only 1 mm in diameter, this discrepancy is not sig-

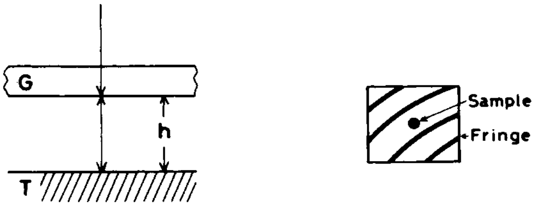

Fig. 5. Principle of operation for measurement of sample thickness.

nificant compared with the thickiness of 10 μm. The sample thickness obtained by this method is accurate to 0.1 μm.

EXPERIMENTAL

Samples. We performed measurements on a urethane acrylate prepolymer (an acrylated polyester urethane from Dainippon Ink and Chemicals Co.) and epoxy acrylate prepolymer (a mixture of trimethylol propane triacrylate and acrylated Epicron 1050 from Dainippon Ink and Chemicals Co.). Photoinitiators were benzoin and acetophenone. It has been a common practice in the UV curing industry to employ a high concentration of photoinitiator to ensure efficient absorption of light. The effect of photoinitiator was examined at concentrations up to 10% by weight.

Measurements. Although the sample thickness was known, it was impossible to determine the shape factor from the weight accurately, because the amount of sample was so small as 0.01 mg. Prior to a series of UV curing experiments, the dynamic viscosity of the prepolymer, $\eta'(0)$, was first determined by using about 50 mg of sample. The area was measured by a microscope and the thickness was determined from the weight. Then the dynamic viscosity $\eta'(t)$ during the UV curing can be obtained from the following equation without measuring the shape factor in each experiment.

$$\eta'(t) = \frac{m(t)\sin\phi(t)}{m(0)\sin\phi(0)}\,\eta'(0) \tag{10}$$

For all runs, the sample thickness was kept at 12 μm and the temperature at 30°C.

RESULTS

Figure 6 shows the dependence of dynamic viscosity on the exposure time for urethane acrylate prepolymer with benzoin at various concentrations. The dynamic viscosity rapidly increases with time after a certain period. The curve

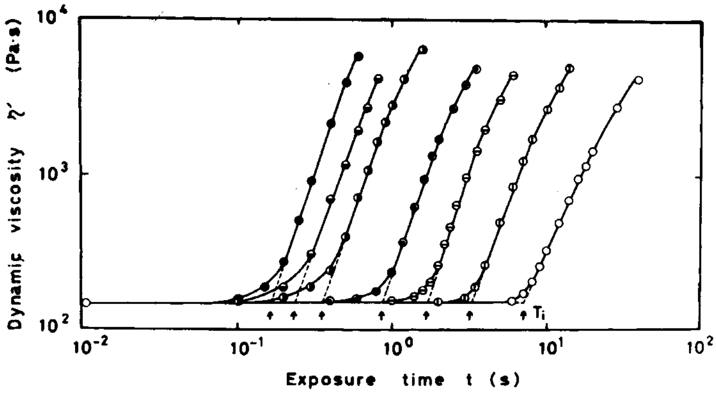

Fig. 6. Dependence of dynamic viscosity on the exposure time for urethane acrylate prepolymer with benzoin (wt %) at various concentrations: (○) 0; (⦶) 0.065; (⊖) 0.23; (⊙) 0.65; (◑) 2; (◒) 5; (●) 10.

can be divided into two regions, and the data in each region can be approximated by a straight line. From these results, the UV curing process has an induction period for photopolymerization. The induction period T_i can be evaluated by the time of the intersection between two lines. There are two remarkable effects of benzoin. First, the induction period decreases with increasing benzoin concentration. Benzoin acts as an effective photoinitiator because the exposure energy required to start the UV curing is markedly reduced. Second, after the induction period, the slope of line is approximately constant irrespective of benzoin concentration. The dynamic viscosity varies as the 3.0 power of the exposure time. Therefore, once the network polymerization starts, the reaction kinetics is not affected by benzoin.

The effect of acetophenone on the UV curing of urethane acrylate prepolymer was also examined. The results are shown in Figure 7. Acetophenone shows the same effect for the induction period as benzoin. However, comparing the results in Figures 6 and 7, the induction periods for prepolymer with acetophenone are shorter than those with benzoin. Acetophenone is a more effective photoinitiator.

The experiments were also performed for epoxy acrylate prepolymer. Figure 8 shows the results for benzoin–epoxy acrylate prepolymer system and Figure 9 for acetophenone–epoxy acrylate prepolymer system. The dependence of dynamic viscosity on exposure time for epoxy acrylate prepolymer is similar to that for urethane acrylate prepolymer.

Figure 10 shows the logarithmic plots of the induction period against the concentration of photoinitiator for all the systems. The relationship for each system can be approximated by a straight line with a slope of -0.6–-0.7. Assuming that decomposition of photoinitiator occurs in proportion to the exposure energy and curing starts when the concentration of radicals originated from photoinitiator reaches a certain level, the data may be correlated by a straight line with a slope of -1. The discrepancy between theoretical and experimental results suggests that self-quenching of radicals occurs to a large extent. The higher the concentration of photoinitiator, the lower the initiation efficiency.

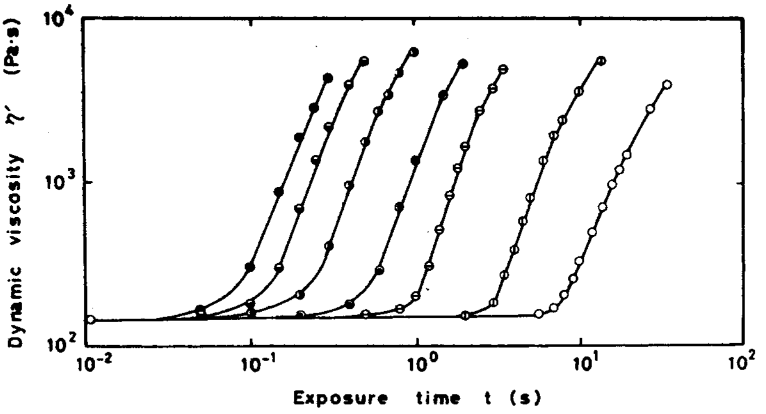

Fig. 7. Dependence of dynamic viscosity of the exposure time for urethane acrylate prepolymer with acetophenone (wt %) at various concentrations: (○) 0; (⦶) 0.057; (⊖) 0.24; (⊙) 0.63; (◑) 2; (◒) 5; (●) 10.

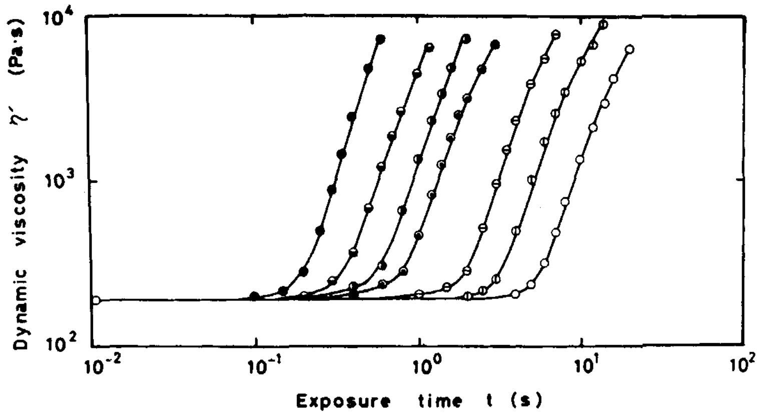

Fig. 8. Dependence of dynamic viscosity on the exposure time for epoxy acrylate prepolymer with benzoin (wt %) at various concentrations: (○) 0; (◐) 0.078; (⊖) 0.28; (⊙) 1; (◑) 2; (●) 5; (●) 10.

Concerning the photosensitizer, increasing the concentration does not always increase the cure rate.[11,12] Acetophenone ensures more efficient absorption of UV light (Fig. 10) than benzoin.

DISCUSSION

Although it was confirmed that the apparatus is very useful, there exists a serious limitation. Since the sensitivity of condenser pickup is relatively low, the amplitude of applied shear should be of the order of 10 μm or more to carry out the experiments precisely, whereas the sample thickness is of the same order. Hence the sample is subjected to a large amplitude of strain, which may cause a nonlinear viscoelastic response. The appearance of nonlinearity tremendously complicates the description of the behavior. The dynamic measurements at different constant strains or stresses are recommended to analyze the nonlinear viscoelasticity, but it is impossible to perform such experiments with the apparatus. The amplitude of sinusoidal force, which is applied to the moving com-

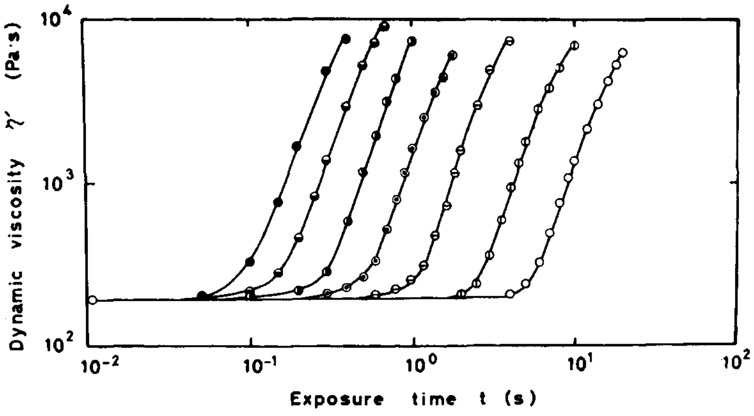

Fig. 9. Dependence of dynamic viscosity on the exposure time for epoxy acrylate prepolymer with acetophenone (wt %) at various concentrations: (○) 0; (◐) 0.052; (⊖) 0.24; (⊙) 0.68; (◑) 2; (●) 5; (●) 10.

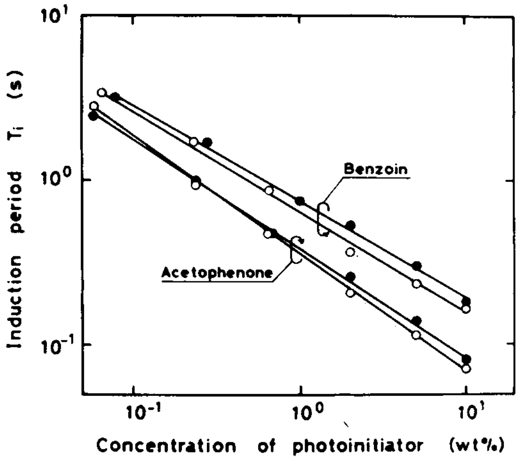

Fig. 10. Dependence of induction period on the concentration of photoinitiator: (○) urethane acrylate; (●) epoxy acrylate.

ponents, is all that can be controlled in the experiments. Both the stress and strain amplitudes vary with time. Therefore, the experimental results are obtained under variable conditions. The problem arises of how to treat the data for nonlinear materials, especially for pigment suspensions such as UV curing inks, because suspensions of fine particles often show nonlinear viscoelasticity even at a strain amplitude of a few percent. However, our apparatus gives a useful and quantitative characterization parameter in the course of UV curing by only one exposure. Supposing that the dynamic viscosity has the same physical meaning as the degree of curing, the rate equation could be derived as a simplified approach. The apparatus is capable of sophisticated experiments which are hardly performed by the conventional method. For instance, how the photopolymerization is affected by a double-step application of UV energy can be studied. These considerations lead to a conclusion that our apparatus is very useful for study of reaction mechanisms of photosensitive polymers.

CONCLUSIONS

The viscoelastic measurements during UV curing were carried out using the newly developed apparatus. Our apparatus has the following advantages:

1. The required amount of sample is extremely small. The measurements can be made even with 0.01 mg of sample.
2. Although the measurements are carried out with liquid polymer, a cell for the sample is not necessary since its surface tension is available.
3. Since the sample thickness is about 10 μm, the temperature can be easily controlled.
4. By measuring the thickness before and after UV irradiation, the volume contraction of sample can be determined.
5. The apparatus may be used for measurement of reaction rates and analysis of reaction mechanisms of photosensitive polymers and thermosetting resins.

The authors are indebted to Mr. Toshiyasu Nishioka for his help in carrying out part of the experiments.

References

1. B. E. Hulme, *J. Oil Color Chem. Assoc.*, **59,** 245 (1976).
2. M. J. Hird, *J. Coatings Technol.*, **48,** 75 (1976).
3. M. D. Garret, *Amer. Ink Maker*, **52**(11), 20 (1974).
4. V. D. McGinniss, "Ultraviolet Curing of Pigmented Coatings," in *Ultraviolet Light Induced Reactions in Polymers*, S. S. Labana, Ed., Amer. Chem. Soc., Washington, D. C., 1976, p. 144.
5. V. D. McGinniss, *J. Rad. Curing*, **2,** 14 (1975).
6. L. Dintenfass, *Rheol. Acta*, **2,** 187 (1962).
7. D. F. Douglas, G. A. Lewis, and A. J. B. Spaull, *Rheol. Acta*, **10,** 382 (1971).
8. J. Mewis and R. de Bleyser, *Rheol. Acta*, **14,** 721 (1975).
9. K. Watanabe, T. Amari, and Y. Kubota, *Rept. Prog. Polym. Phys. Japan*, **22,** 99 (1979).
10. H. Wakeshima, Patent pending (Japan).
11. Y. C. Chang, *Photogr. Sci. Eng.*, **21,** 348 (1977).
12. M. W. Wolf, R. E. Brown, and L. A. Singer, *J. Am. Chem. Soc.*, **99,** 526 (1977).

Received February 17, 1983
Accepted July 6, 1983