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- (20) An additional condition for these systems to be described by the theory of section 2 is that the approximation by which we treat  $L$  as a continuous variable be applicable. During the process of waiting for a nearby break, a total arc length of order  $L^* \cong (D_0 \tau)^{1/2} \cong \bar{L}^{3/4}$  passes through any tube segment. Hence, for self-consistency, we require only that the individual functionalized polymers that make up the longer chains have length  $L_0 \ll L^*$ . If this is not the case, one expects instead a longer relaxation time,  $\tau \cong D_0^{-1} \bar{L} L_0^2$ , corresponding to a rate-limiting step that involves a given tube segment waiting for one of the junction points—at which breakage is comparatively frequent—to reapeat past.

## Holographic Grating Relaxation Measurements of Dye Diffusion in Linear Poly(methyl methacrylate) and Cross-Linked Poly(methyl methacrylate) Hosts

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**ABSTRACT:** Laser-induced holographic grating relaxation studies of camphorquinone (CQ) diffusing in linear poly(methyl methacrylate) (PMMA) and cross-linked PMMA are carried out. Diffusion coefficients of CQ in the polymer hosts are derived from the decay constant of the intensity diffracted from the laser-induced holographic grating. The diffusion coefficient ( $D$ ) of the photoproduct of CQ in cross-linked PMMA is found to decrease about 2 orders of magnitude as the concentration of the cross-linking agent increases to 50%. The relationship between the concentration of the cross-linking agent and polymer-free volume is discussed. The diffusion coefficients in linear and cross-linked PMMA are also measured as functions of temperature ( $T$ ). The temperature dependence of  $D$  can be described by the Williams-Landel-Ferry (WLF) equation. The  $C_2$  constant obtained from the  $D$  vs.  $T$  fit for the linear PMMA sample agrees with that from the viscosity measurement.

### Introduction

In our previous work,<sup>1</sup> we have reported the study of the diffusion process of camphorquinone (CQ) in linear and cross-linked polystyrene (PS) using the holographic grating relaxation technique. In this paper, we report results of the study of the diffusion process of CQ in linear and cross-linked poly(methyl methacrylate) (PMMA) by using the same technique.

The laser-induced holographic grating relaxation (LIHGR) technique has been shown to be capable of measuring a very slow diffusion coefficient of photochromophores dissolved in transparent polymer hosts in the vicinity of their glass transition temperatures. This technique involves splitting of a single-frequency radiation from an  $\text{Ar}^+$  laser radiation into two equal-intensity beams. Interference of two beams induces a holographic phase grating by photobleaching the dye molecules. In the present study, the distance between bright and dark fringes ( $d/2$ ) is varied between 0.84 and 11.62  $\mu\text{m}$  by changing the crossing angle of the two beams. Diffusion of the dye molecules over a length less than  $d/2$  is detected imme-

diate as it reduces the diffracted intensity. Since  $t = d^2/(4\pi^2 D)$  ( $t$  being the time of diffusion and  $D$  the diffusion coefficient), and since the diffusion distance  $d$  involved in the LIHGR technique is on the order of the wavelength of the writing beam, the LIHGR technique can be employed to obtain the diffusion coefficient several (up to 8) orders of magnitudes smaller than the slowest  $D$  that the conventional tracer technique can provide. Applying this technique, it is possible to measure the mass diffusion coefficients as low as  $10^{-15} \text{ cm}^2/\text{s}$  in a period of several hours.

Recent LIHGR works reported from our laboratory differ from the LIHGR studies carried out elsewhere in that chromophore molecules are not chemically attached to the polymer chains. In our work, foreign dye molecules are introduced in the polymer matrices without modifying the polymer chains. The dye molecules (or penetrants) are introduced only in a trace amount (on the order of 1% or less by weight). The frictional resistance that the penetrants encounter during diffusion serves to monitor that experienced by the polymer segments themselves in

their random motion. At the vanishing concentration of the penetrants, the mass diffusion coefficient  $D$  of the penetrant is related to the monomer friction coefficient  $\xi$  of the polymer chain by  $\xi = (kT)/D$ .<sup>4</sup>

In the previous work, we showed that diffusion of CQ in linear PMMA and in poly(*tert*-butyl methacrylate) (PtBMA) hosts above the glass transition temperature ( $T_g$ ) is basically determined by the dynamics of the polymer chains.<sup>2</sup> We also showed that cross-linking of the polymer chains reduces the average free volume (increases the friction coefficient) and, hence, reduces the diffusion rate of the penetrants.<sup>1</sup>

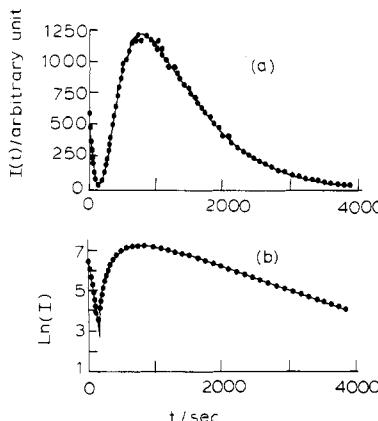
Our objectives in the present study are as follows: (1) to further examine the relationship between the diffusion coefficient of CQ and the concentration of cross-linking agent by measuring the diffusion coefficient of CQ in PMMA with different concentrations of cross-linking agent; (2) to relate the diffusion coefficient to the viscoelasticity data by fitting the temperature dependence of  $D$  to the WLF equation in order to examine the dynamics of the diffusion process.

## Experimental Section

Linear and cross-linked PMMA are synthesized in our laboratory with the free radical polymerization method. Pure MMA monomers are purchased from the Aldrich Co. and purified by vacuum distillation (to remove inhibitors). The purified MMA is added with 0.1% initiator [2,2-azobis(2-methyl-propionitrile)] and 1% CQ (by weight) into a 500-cm<sup>3</sup> beaker and stirred well. The solution is then distributed in eight test tubes (o.d. = 11.5 mm), each containing different amounts of the cross-linking agent (bisphenol A dimethacrylate). The test tubes are then sealed with a flame and put in an oven for polymerization. Eight yellowish, transparent solid rods are obtained after about 5 days of polymerization (24 h at 50 °C, 24 h at 80 °C, 24 h at 96 °C, 24 h at 114 °C, 24 h at 133 °C, 5 h at 145 °C). Another linear PMMA sample is prepared by carrying out polymerization for 14 days, with temperature varying from 40 to 170 °C in a 10 °C per 24 h step. To determine the soluble fraction of the cross-linked polymer, the sample with a given concentration of the cross-linking agent is fluxed with tetrahydrofuran for about 48 h. The weight of the sample before and after the flux is then compared. We have found that all cross-linked samples contain no soluble fraction.

Slices are cut from the rods and polished into pellets having a thickness of 2–3 mm. The pellets (one at a time) are mounted in a specially designed copper holder which is then placed in a temperature-controlled oven with glass windows to permit transmission of laser beams. After thermal equilibrium is reached, a holographic phase grating is induced by crossing two equal intensity writing (bleaching) beams splitting from the main beam of an Ar<sup>+</sup> laser operating at  $\lambda = 4880 \text{ \AA}$ . This experimental setup is similar to that described in ref 3, except that the photodiode is replaced by a photomultiplier and the picoammeter is replaced by a lock-in amplifier combination to improve both the detection sensitivity and the signal-to-noise ratio. The angle between the bleaching beams is varied from  $\theta = 2.54^\circ$  to  $\theta = 35.67^\circ$  so the grid spacing  $d = \lambda/[2 \sin(\theta/2)]$  ( $\lambda$  being the wavelength of the laser radiation in vacuum) varies from 11.62 to 0.84  $\mu\text{m}$ . This ensures that the relaxation time  $\tau = d^2/(4\pi^2 D)$  ( $D$  is the diffusion coefficient of the dye) falls into a conveniently measurable range of our experimental setup. The laser radiation used at the sample is about 10 J/cm<sup>2</sup>. After the grating is induced, one of the bleaching beams is shuttered off and the other is immediately attenuated by a factor of 100–10000. The attenuated beam serves as a reading beam which is diffracted by the induced grating to the photodetector, according to the Bragg condition. The diffracted intensity (measured in the first order) decays, owing to the onset of the relaxation process. Thus, the relaxation time can be deduced from the time dependence of the diffracted intensity curve. The attenuation of the reading beam is necessary in order to avoid any further photobleaching of the exposed sample.

The photochemistry of CQ involves the hydrogen abstraction initiated from the induced photochemical reaction; its influence



**Figure 1.** (a) Diffracted intensity  $I(t)$  as a function of time,  $t$ , of pMMA + 1% CQ at  $T = 122$  °C. (b) Logarithm of the diffracted intensity given above plotted vs. time. Note that the decay at long times portion appears linear in this plot.

on the polymer matrices have been discussed elsewhere.<sup>3</sup> The disturbance to the structure of the polymer matrix due to the H atom abstraction is negligible.

## Results and Discussion

Although the LIHGR technique basically measures the mutual diffusion coefficient when the concentration of the dye in the dye–polymer system is sufficiently low, the mutual diffusion coefficient reflects the monomer diffusion coefficient of the polymer chain.<sup>4</sup> In the present experiment, the dye concentration used is 1% or less by weight. In the following discussion, we will discuss the monomer diffusion in terms of the mutual diffusion of the photochromous dye.

A typical diffracted light intensity vs. time ( $I(t)$  vs.  $t$ ) that is observed is shown in Figure 1a. The diffracted intensity curve consists of a rapid decay portion at short times, followed by a growth portion and then a slow decay at long times. This curve shape has been shown to arise from diffusive relaxation of two sets of holographic gratings. One set is due to the refractive index modulation associated with unreacted CQ in the dark fringe area and the other with its photoproduct in the bright fringe area.<sup>2</sup> The intensity curve as a function of time has been shown to fit the equation<sup>3</sup>

$$I(t) = (Ae^{-t/\tau_1} - Be^{-t/\tau_2})^2 \quad (1)$$

When the curve is presented in the  $\ln [I(t)]$  vs.  $t$  plot (Figure 1b), the decay portion at long times appears to be linear for all samples studied at all temperatures. In eq 1,  $\tau_1$  is the relaxation time constant associated with the diffusion of the unbleached CQ molecules and  $\tau_2$  is that associated with its photoproduct (CQP). The slope ( $s$ ) of the linear long times portion in the  $\ln [I(t)]$  vs.  $t$  plot is related to  $\tau_2$  by  $\tau_2 = |2/s|$  which is, in turn, related to the diffusion coefficient ( $D$ ) of CQP by

$$\tau_2 = d^2/(4\pi^2 D) \quad (2)$$

where  $d$  is the grid spacing of the induced holographic grating. In ref 3, we showed that virtually identical diffusion coefficients of CQP are obtained either by measuring the slope or by fitting the  $I(t)$  vs.  $t$  curve to eq 1; the latter method takes considerably more computer time despite the fact that the diffusion coefficients of CQ and CQP can be simultaneously determined by using this method.<sup>5</sup>

The work reported in ref 1 shows that CQ and its photoproduct are thermally stable and that no thermal reverse reaction (CQP to CQ) has occurred at  $T = 128$  °C. Mea-

**Table I**  
**Diffusion Coefficients of Linear and Cross-Linked PMMA**  
**at Various Temperatures**

linear ( $x = 0$ )	cross-linked ( $x = 0.15$ )	linear ( $x = 0$ )	cross-linked ( $x = 0.15$ )
$T/K$	$D/cm^2 s^{-1}$	$T/K$	$D/cm^2 s^{-1}$
388.9	$1.64 \times 10^{-14}$	405.4	$1.56 \times 10^{-13}$
393.5	$8.5 \times 10^{-14}$	409.5	$6.58 \times 10^{-13}$
396.0	$1.93 \times 10^{-13}$	414.9	$2.04 \times 10^{-12}$
401.2	$5.89 \times 10^{-13}$	418.2	$4.76 \times 10^{-12}$
405.1	$1.37 \times 10^{-12}$	423.0	$1.90 \times 10^{-11}$
409.6	$3.84 \times 10^{-12}$	427.2	$2.91 \times 10^{-11}$
414.2	$8.95 \times 10^{-12}$	431.7	$5.34 \times 10^{-11}$
418.7	$1.78 \times 10^{-11}$	437.2	$1.04 \times 10^{-10}$
423.3	$3.55 \times 10^{-11}$	442.8	$3.49 \times 10^{-10}$
427.8	$6.05 \times 10^{-11}$		
432.3	$1.00 \times 10^{-10}$		
436.9	$1.71 \times 10^{-10}$		
441.4	$2.54 \times 10^{-10}$		
446.0	$3.64 \times 10^{-10}$		

**Table II**

**Variation of the Glass Transition Temperature ( $T_g$ ) with the Concentration  $x^a$**

$x$	$T_g/^\circ\text{C}$	$x$	$T_g/^\circ\text{C}$
0%	117.8	20%	144.0
5%	125.0	30%	152.8
10%	131.3	40%	158.8
15%	137.3	50%	<i>b</i>

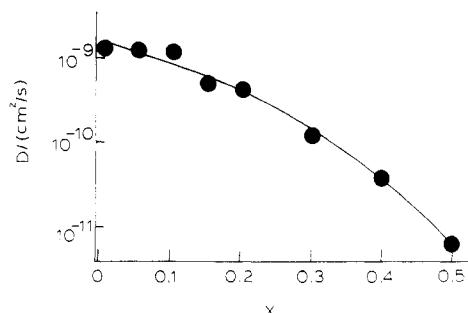
<sup>a</sup> Weight of the cross-linking agent/weight of pure PMMA.  
<sup>b</sup> The glass transition range is too broad to obtain a meaningful value of  $T_g$ .

surements reported in the same work also show that the WLF equation can be applied to account for the temperature dependence of the diffusion coefficient at temperatures in the range 110–163 °C. The result suggests that CQ and CQP are thermally stable up to at least 163 °C.

For  $T > T_g$ , free volume theory provides a satisfactory description of the diffusion process. The basic idea of the free volume theory for diffusion of small molecules in a polymer host is that diffusion is facilitated by the cooperative motion of the polymer segments, that is, a diffusant is assumed to vibrate about its equilibrium position until the combination of two events occurs, this combination being (1) the molecule attains sufficient energy to overcome the attractive potential holding it to its neighbors and (2) a large enough void (free volume) is created (through the cooperative motion of the polymer segments near the diffusant) into which it can jump. It has been shown that at vanishing solute concentrations and at temperatures not much higher than  $T_g$  ( $T_g < T < T_g + 100$  °C), the second process is a determining factor.

Introduction of chemical cross-linking into linear polymer chains significantly affects the average size of free volume and hence the friction coefficient of the penetrant. Introducing the cross-linking agent greatly increases the rigidity of the polymer and, hence, increases its glass transition temperature. The variation of the glass transition temperature with concentration of the cross-linking agent is given in Table II. If the cross-linking process is not accompanied by side reactions which significantly alter the chemical nature of the polymer, the decrease in the diffusion coefficient may be completely attributed to a decrease in the fractional free volume as a result of formation of the cross-links.

Although the cross-linking agent may increase free volume due to dilution, it decreases the size of free volume by reducing big voids into smaller ones; the latter apparently has a much larger effect. The dependence of  $D$  on the concentration of the cross-linking agent in the 0–50% (by weight) range is shown in Figure 2 in the  $\ln D$  vs.  $x$



**Figure 2.** Logarithm of the diffusion coefficient ( $D$ ) of CQ in cross-linked PMMA plotted as a function of the concentration of the cross-linking agent,  $x$  ( $x$  = weight of the cross-linking agent/weight of monomer). The data are obtained at  $T = 173$  °C.

plot, where  $x$  denotes the concentration of the cross-linking agent.

Since all cross-linked samples contain no soluble polymer fraction, we assume that all the cross-linking agents are used to form cross-linking bonds; one expects that the fractional decrease in free volume is proportional to the increase of the concentration of the cross-linking agent. Namely,

$$\frac{dV_f(x)}{V_f(x)} = -\alpha dx \quad (3)$$

which is integrated to yield

$$V_f(x) = V_f(0)e^{-\alpha x} \quad (4)$$

where  $\alpha$  is a parameter whose amplitude determines the effectiveness of the cross-linking agent on reducing the average free volume;  $V_f(x)$  and  $V_f(0)$  are free volume at  $x$  and at  $x = 0$ , respectively. Since the dye diffusion coefficient is related to the free volume  $V_f$  by<sup>6</sup>

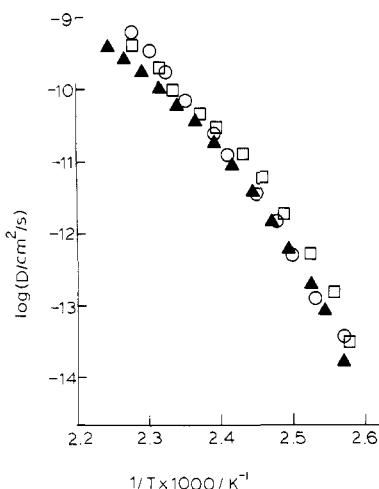
$$\ln D = \ln D_0 - V^*/V_f(0) \quad (5)$$

where  $D_0$  is the pre-exponential factor representing the asymptotic diffusion coefficient at high temperature.  $V^*$  is the minimum or the critical size of free volume required for the molecule to make a jump. An elaboration of eq 5, which details the diffusion process of penetrants in a polymer host, has equated  $V^*$  to  $\nu \hat{V}_2^* \xi$ .<sup>7</sup> Here,  $\nu$  is a numerical factor introduced to correct for the overlap of free volumes between 0.5 and 1;  $\xi$  is the ratio of the volume of the penetrant to the volume of the polymer jumping unit.  $\hat{V}_2^*$  is the critical size of free volume in the polymer which is required to accommodate the diffusant. If the introduction of the cross-linking agent decreases  $V_f(0)$  to  $V_f(x)$ , in the manner described by eq 4, we may replace  $D$  by  $D(x)$  and  $V_f(0)$  by  $V_f(x)$  in eq 5. This then yields (setting  $V^* = \nu \hat{V}_2^* \xi$  in accordance with ref 7)

$$\ln D(x) = \ln D_0 - \frac{\nu \hat{V}_2^* \xi}{V_f(0)} e^{\alpha x} \quad (6)$$

If  $\alpha x$  is much less than one, one may approximate  $e^{\alpha x}$  by  $(1 + \alpha x)$ . In this case,  $\ln D(x)$  will linearly decrease with increasing  $x$  when  $x$  is smaller than  $\alpha^{-1}$  as is the case for cross-linked polystyrene which is recently reported.<sup>1</sup> At larger  $\alpha$  or larger  $x$  such that  $\alpha x > 1$ ,  $\ln D(x)$  will decrease nonlinearly with increasing  $x$ . This is observed in the present system.

We have fitted the experimental data points at 173 °C, which are shown in Figure 2, to eq 6 and have obtained the following parameters:  $\ln D_0 = -18.27$  (or  $D_0 = 1.16 \times 10^{-8} \text{ cm}^2/\text{s}$ ),  $\nu \hat{V}_2^* \xi / V_f(0) = 2.02$ , and  $\alpha = 2.62$ . The fit of the experimental data to eq 6 is satisfactory. Since the

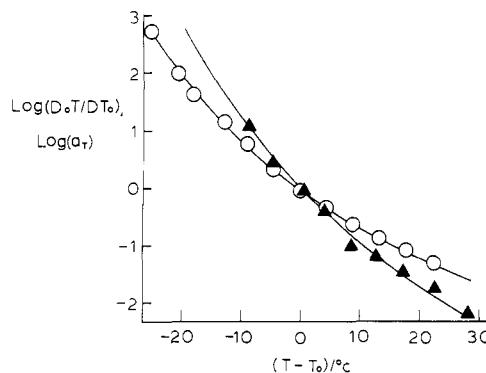


**Figure 3.** Comparison of the temperature dependence of the diffusion coefficient of CQ in nearly monodispersed PMMA and polydispersed PMMA: (○) sample with 5 days of polymerization; (□) sample with 14 days of polymerization; (▲) commercial sample.

same cross-linking agent is used in both PMMA and PS, we can compare its effects on both polymers. Upon increasing the concentration of the cross-linking agent  $x$  from 1% to 20% (by weight), the diffusion coefficient in PS decreases approximately 30 times, whereas in PMMA it decreases only 3 times. However, at  $x = 50\%$ , the mass diffusion coefficient of CQ in PMMA decreases about 200 times from  $1.05 \times 10^{-9}$  to  $6.67 \times 10^{-12} \text{ cm}^2/\text{s}$ . (Over the concentration range studied, the decrease in PMMA is nonlinear.) Such a decrease in  $D$  stems from the exponential decrease in the size of free volume as  $x$  increases. Thus, although the retardation effect of the cross-linking agent, bisphenol A dimethacrylate, on the diffusion process of CQ in PMMA is slow initially, it becomes drastic as the concentration of the cross-linking agent becomes appreciable. This result is different from that of PS as the cross-linking agent affects its dye diffusion coefficient only in a linear fashion.<sup>1</sup>

It should also be noted that the value of the combined parameters  $\nu \hat{V}_2^* \xi / V_f(0)$  is equal to 2.02. Since both  $\xi$  and  $\nu$  are less than 1, it implies that  $V_f(0) < \hat{V}_2^*$ . This suggests that there is a significant distribution of free volume with a size smaller than the critical free volume  $\hat{V}_2^*$ . Because of the presence of a large population of free volume with sizes less than  $\hat{V}_2^*$ , cooperative segmental motion of polymer chains must be required to allow for diffusion to occur.

Comparison of the diffusion coefficients of CQ in polydispersed PMMA with that in nearly monodispersed PMMA at various temperatures is presented in Figure 3. The nearly monodispersed PMMA is a commercially available sample with  $M_w/M_n = 1.76$  and  $M_w = 460\,000$ . The polydispersed samples are polymerized in our laboratory. Two types of polydispersed samples are used: one using 5 days and the other 14 days to complete the polymerization. The one that takes 5 days for polymerization has a  $M_w/M_n = 2.4$  and  $M_w \approx 240\,000$ , as determined by GPC. Our thermal analysis data obtained with Perkin-Elmer Delta DSC 7 system show the onset of the glass transition at 112 °C and the midpoint at 119 °C. Molecular weight of the other sample that takes 14 days to polymerize are not characterized but are expected to contain no monomers and to have a different molecular weight distribution. The DSC data of this polymer is quite similar to that given above, with the onset temperature equal to 110 °C and the midpoint at 116 °C. One notes that over the entire temperature range, the two sets of data obtained



**Figure 4.** Shift factors obtained from the diffusion data of PMMA and PMMA containing 15% cross-linking agent. The dots are experimental points and lines are fitted curves.

with our own polymerized samples differ by a shift of approximately 3 K. Further, below  $T = 417$  K, the data obtained for the monodispersed sample and those of the polydispersed samples are similar. Above 417 K, the monodispersed sample has a smaller diffusion coefficient. The difference corresponds to a temperature shift of about 3 K above 417 K. This could easily be caused by the temperature gradient in the sample holder used in our previous work.<sup>2</sup>

The diffusion coefficients of CQ in linear PMMA and in cross-linked PMMA at various temperatures are given in Table I. The temperature dependence of the diffusion coefficient of both the cross-linked and uncross-linked PMMA samples is not Arrhenius. Consistent with the free volume description of the diffusion process is the Williams-Landel-Ferry (WLF) equation which is often used to describe the temperature dependence of viscoelastic data.<sup>4</sup> In a previous paper,<sup>2</sup> we have reported the fit of the diffusion data of a nearly monodispersed PMMA to the WLF equation given by

$$\ln [D(T)/D(T_g)] = \frac{2.303C_1(T - T_g)}{C_2 + T - T_g} \quad (7)$$

where  $D(T_g)$  is the diffusion coefficient measured at  $T_g$ ;  $C_1$  and  $C_2$  are the WLF coefficients for diffusion. For the uncross-linked PMMA sample, we obtain  $C_1 = 8.22$  and  $C_2 = 54.24$  K which are already reported in ref 2.

The relation of the friction coefficient  $\xi_1$  to the fractional free volume ( $f$ ) is given by<sup>8</sup>

$$\ln \xi_1 = \text{const} + B/f \quad (8)$$

Ferry has shown<sup>4</sup> that if the temperature range is sufficiently high to apply the WLF equation, a proper equation representing the temperature shift factor  $\log a_T$  is

$$\begin{aligned} -\log a_T &\equiv \log (D(T)/D(T_g)) = \\ &C_1^D(T - T_g)/(C_2^D + T - T_g) \quad (9) \end{aligned}$$

rather than eq 7.

Shown in Figure 4 (lines) are the shift factors and the fits of the diffusion data of PMMA and of 15% cross-linked PMMA to eq 9. The reference temperature  $T_0$  and the diffusion coefficient  $D_0$  (at  $T_0$ ) used are  $T_0 = 414.2$  K,  $D_0 = 1.73 \times 10^{-11} \text{ cm}^2/\text{s}$  for linear PMMA and  $T_0 = 414.9$  K,  $D_0 = 2.04 \times 10^{-12} \text{ cm}^2/\text{s}$  for the 15% cross-linked PMMA. The  $D_0$  values are the measured data at  $T_0$ .

In this work, rather than choosing  $T_g$ , we choose the reference temperature  $T_0$  at 414.9 K because the diffusion coefficient at  $T_0$  is subject to less uncertainty. The diffusion coefficient at  $T_g$  generally takes several hours to measure. During these long times, laser intensity fluctuations as well as the effect of physical aging would make

the value of the diffusion coefficient uncertain.<sup>9</sup> As seen in Figure 4, all of the diffusion data are well represented by eq 9. However, since the effect of temperature on  $D$  is large, we have found that eq 7 also gives a good fit to the diffusion data. The fit gives a similar  $C_2$  value when the same reference temperature is used. The WLF constants obtained are  $C_1^D = 5.46$  and  $C_2^D = 80.3$  K for the uncross-linked sample and  $C_1^D = 8.70$  and  $C_2^D = 83.7$  K for the 15% cross-linked sample.

The  $C_2^D$  value obtained by using eq 9 agrees, within experimental uncertainty, with that extracted from the shear creep data of atactic PMMA by Plazek et al.<sup>10</sup> ( $C_2 = 80$  K). The value of  $C_1^D$  differs from the  $C_1$  value obtained from the creep data<sup>8</sup> ( $C_1 = 14$ ). This is expected, as the minimum void size in the sense of free-volume theory for the diffusant-polymer system is not the same in relation to the size of the moving unit underlying the creep experiment. The fact that  $C_1^D/C_1 = 5.46/14 = 0.39$  is consistent with results of the comparison previously obtained.<sup>4</sup> In terms of the interpretation developed in ref 7, this ratio indicates that the size of CQ is only about 39% the volume of the polymer jumping unit. Note that, in contrast to the PS result,  $C_2^D$  for the cross-linked sample is less than of  $C_2^D$  in the uncross-linked polymer. Since there is a decrease in the thermal expansion coefficient of the cross-linked sample, the decrease in  $C_2^D$  for the cross-linked PMMA is apparently associated with the decrease of the free volume which outweighs the decrease of thermal expansion coefficient.<sup>4</sup>

In summary, we have measured the diffusion coefficients of camphorquinone in linear PMMA and cross-linked PMMA. Over 0-50% (by weight) of the cross-linking

agent concentration, the diffusion coefficient of CQ decreases drastically with increasing concentration of the cross-linking agent. The result can be satisfactorily interpreted in terms of free volume theory. The result of temperature-dependent studies is consistent with free volume theory. The diffusion coefficient appears to be insensitive to the molecular weight distribution. The WLF constants extracted from either plot are in agreement with those obtained from the viscoelastic data.

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**Registry No.** CQ, 465-29-2; PMMA, 9011-14-7; (bisphenol A dimethacrylate)(MMA) (copolymer), 31547-90-7.

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## Relaxation by Constraint Release in Combs and Star-Combs<sup>†</sup>

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**ABSTRACT:** A number of polybutadiene combs and 4- and 18-arm star-combs have been prepared. They have been characterized by their dilute solution properties. The viscoelastic properties of their melts have been investigated over a wide range of frequencies and temperatures. The maximum in  $G''(\omega)$  in the plateau zone has been correlated with a similar maximum in  $G''(\omega)$  of regular stars and is attributed to the equilibration of the branches. The low-frequency behavior of  $G''(\omega)$  and  $G'(\omega)$  is Rouse-like. The experimental longest relaxation time ( $\tau_1$ ) depends exponentially on the branch length. Comparison of  $\tau_1$  for combs and star-combs suggests that  $\tau_1$  depends also on the square of the number of entanglements per backbone. These dependencies are consistent with relaxation of the backbone by constraint release.

## Introduction

At least three classes of branched polymers are distinguished. Star polymers with a single branch point are the simplest. They are widely studied and have specific practical applications. Comb polymers have a linear backbone from which branches emanate. A large class of branched polymers have a randomly branched or treelike structure. They contain no clearly defined backbone and each branch in turn may carry branches.

In order to push the complexity of well-characterized branched polymers beyond that of comb polymers, star-combs have been prepared. Branches are grafted onto the

arms of anionically prepared regular stars. The arms of the parent star and the branches have narrow MW distributions. The number of arms in the star ( $f$ ) is fixed but the number of branches per molecule ( $\bar{p}$ ) has a small distribution. The complexity of these polymers lies between that of combs and randomly branched polymers. Their architecture mimics to some extent the soft sphere polymers which have been described theoretically.<sup>1</sup> The polymer segments can be varied and are generally much looser and less regular than in the starburst-dendritic molecules.<sup>2</sup>

The synthesis and purification of polybutadiene star-combs are described. The polymers are characterized by their dilute solution properties. Some ordinary polybutadiene combs are included for comparison. Special

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