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Photon Correlation Spectroscopy of Polystyrene in the Glass Transition Region

H. Lee, A. M. Jamieson,* and R. Simha

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. *Received December 11, 1978*

ABSTRACT: The dynamic characteristics of the light scattered by atactic polystyrene in the temperature range 92–110 °C are determined by digital photon correlation spectroscopy. Two discrete relaxation processes are present. A slow mode can be represented by an asymmetric Williams–Watts distribution of relaxation times and is essentially identical to that observed by Patterson et al. in the depolarized light-scattering spectrum. A fast process is well defined by a single exponential decay. The characteristic mean relaxation times are compared with the conventional relaxation map for polystyrene, as obtained by dynamic mechanical and dielectric techniques. Concordance between mechanical and photon correlation results in respect to the glass transition process is observed. While the activation energies are also identical with those derived from dielectric data, the characteristic frequencies are lower by two orders of magnitude. As for the β process, the derived activation energy of about 15 kcal/mol is in the range of general expectation, but lower by a factor of 2 than most of the mechanical information reported in the literature. Photon correlation techniques employing both the anisotropic and isotropic components appear to be powerful tools for dynamic relaxation spectroscopy in the glassy state.

Photon correlation spectroscopy has become a well-established technique for examining the hydrodynamic behavior of concentration fluctuations in polymer solutions.[1-5] Subsequently, investigators have successfully applied this probe to study the dynamics of structural relaxation in viscous liquids[6] and inorganic glasses.[7,8] More recently, interest has developed in applying the method to characterize the relaxational behavior of configurational fluctuations of bulk polymers.[9-11] Discrete fast and slow exponential decay processes have been reported in the isotropic light-scattering component of poly(methyl methylacrylate).[9,10] It was concluded that the slow process is related to the glass transition relaxation, while the fast mode is due to side-chain reorientation.[9,10] The depolarized Rayleigh spectrum of polystyrene in the melt near the glass transition temperature has been extensively studied by Patterson et al.[11] A very wide distribution of relaxation times covering five decades of time is observed which is accurately characterized by the Williams–Watts function[12]

$$\phi(t) = \alpha \exp[-(t/\tau_0)^{\beta}] \qquad (1)$$

where α, τ_0, and $0 < \beta \leq 1$ are adjustable parameters. The depolarized spectrum of polystyrene is characterized by an average relaxation time and an activation energy which are stated to be in the range observed by other dynamic relaxation methods for the glass–rubber transition in polystyrene.[11]

In this paper we report a study of the relaxation spectrum of the total intensity of light scattered by polystyrene over a similar range of temperatures. In these experiments, we detect the superposition of the isotropic and depolarized scattering components. Two discrete relaxation modes appear to be present: a slow mode identical to that reported by Patterson et al.,[11] and a single exponential decay which is two orders of magnitude faster than the former.

Experimental Section

(a) Sample Preparation. Monomer styrene was obtained from Aldrich Chemical Co., containing 10–15 ppm of *p-tert*-butylcatechol as inhibitor. The latter was removed by washing with aliquots of 20% NaOH solution and water, and the monomer

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was subsequently dried with anhydrous $CaSO_4$. Polystyrene was prepared by thermal polymerization of Millipore-filtered Tyndall-free monomer at 120 °C for 3 days. The sample was then degassed in a vacuum oven at ca. 120 °C for 1 week. Based on these conditions[13] the polymer is expected to have a molecular weight of about 2×10^5. The sample was then optically polished sequentially using slurries of tungsten carbide and alumina powders of different sizes to produce a cylindrical prism, essentially free of elastic scattering from nonthermodynamic inhomogeneities.

(b) Instrumentation. The experiments reported below were performed on a digital photon correlation spectrometer incorporating a Spectraphysics Model 120 15 mW He/Ne laser source (λ_0 = 6328 Å), an ITT FW 130 phototube, Pacific Photometric Instruments Model 2A33-D6 pulse amplifier/discriminator system, and a Saicor 42A 100 channel digital autocorrelator. Incident light is vertically polarized with respect to the scattering plane and focussed into the scattering volume by a lens, followed by a 500 μm pinhole. Scattered light is passed through a narrow band-pass interference filter ($\simeq$100 Å), centered at the incident laser line, to reduce unwanted background radiation. Amplified pulses from the phototube are analyzed with the Saicor correlator which generates the full autocorrelation function[1-4]

$$C(t) = \langle n(t) \times n(0) \rangle / \langle n \rangle^2 \tag{2}$$

where $n(t)$ is the number of scattered photocounts at time t after the initiation of the light-scattering experiment, and $\langle n \rangle$ is the average count rate over the duration of the experiment. The Saicor correlator has a variable sampling increment, ranging from 0.5 μs to 1 s. It can therefore be used to observe relaxation processes of amorphous polymers when the average relaxation times range from 10^{-5} to 100 s.

The full photon autocorrelation function is related to the relaxation spectrum $\phi(t)$ by the equation[1-4]

$$C(t) = 1 + f(A)\phi^2(t) \tag{3}$$

where $f(A)$ is a spatial coherence factor which depends on the number of coherence areas observed in the sample volume and the sampling increment. Most earlier quasielastic light-scattering studies of glassy systems have determined the clipped photon correlation functions.[1-4] As long as the scattering phenomena exhibit Gaussian random fluctuation behavior, either correlation function would contain equivalent information.

(c) Data Analysis. The photon correlation technique observes the relatively slow relaxational components in the scattered light. Fast processes which primarily include thermal diffusion and the Brillouin phonon modes[1-4] are not detected. In the experiments described here, with the incident light polarized vertically, and all of the scattered light detected, approximately $^1/_3$ of the radiation represents isotropic scattering, the remaining $^2/_3$ being anisotropic scattering.[14] The characteristics of the latter contribution have recently been studied by Patterson et al.[11] and are due to the orientational fluctuations of chain units. The isotropic scattering has been likened to a longitudinal stress relaxational experiment at constant longitudinal strain,[6-8] and its dynamic properties are determined by the relaxational components of the compressional and shear moduli.

In our observations, the measured $C(t)$ is therefore of the form

$$C(t) = 1 + f(A)[\phi_{\text{orient}}(t) + \phi_{\text{relax}}(t)]^2 \tag{4}$$

Previous light-scattering studies of glasses[6-8,11] by correlation spectroscopy have employed the Williams–Watts function, eq 1, to interpret $\phi(t)$. In principle, this function can be related to the associated distribution of relaxation times in the system, viz.:

$$\phi(t) = \int_0^{n} e^{-t/\tau'} \rho(\tau') \, d\tau' \tag{5}$$

In practice, it is not yet feasible to derive $\rho(\tau')$ from the experimental $\phi(t)$. As a critical test of the utility of the Williams–Watts function, we examine our correlation functions in the representation

$$\log \left\{ -\frac{1}{2} \ln \frac{[C(t) - 1]}{f(A)} \right\} = -\beta \log \left(\frac{t}{\tau_0} \right) \tag{6}$$

The characteristic constants β and τ_0 can be determined from the slope and intercept of a plot of the left-hand side of eq 6 vs. log t. The parameter β decreases from a value of unity as the width of the distribution increases. The mean relaxation time $\langle \tau \rangle$ is derived from

$$\langle \tau \rangle = (\tau_0/\beta)\Gamma(1/\beta) \tag{7}$$

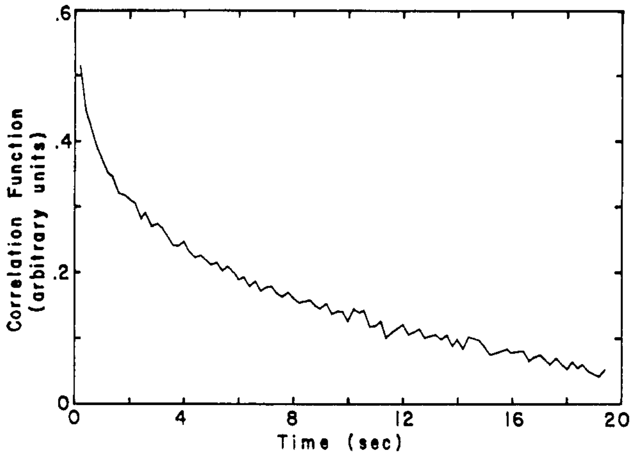

Figure 1. Full photon correlation function of light scattered at $\theta = 90°$ by atactic polystyrene at $T_g = 96.7 \pm 0.5$ °C in the range of 0 to 20 s.

Table I
Characteristic Relaxation Parameters

T, °C	β_1	τ_1, s	$\langle\tau_1\rangle$, s	β_2	τ_2, ms	$\langle\tau_2\rangle$, ms	$\alpha_2/(\alpha_1 + \alpha_2)$
96.7	0.38	18.5	71.6	0.96	3.4	3.4	0.034
102.8	0.40	0.89	2.87	0.97	1.9	1.9	0.038
107.0	0.40	0.21	0.70	1.00	2.0	2.0	0.055
111.5	0.40	0.035	0.12	1.00	0.79	0.79	0.067

In the experiments discussed below, we have not attempted to compute the exact numerical values of the $\phi(t)$ but are concerned with describing the characteristic shapes of the relaxation functions. We have therefore normalized our experimental function $C(t)$ to unity, but note in agreement with Patterson et al.[11] that a major contribution to the dynamics of the total scattered light, about 65%, is present at very short times, outside the detection range of the Saicor correlator. This in no way affects the principal conclusion of our work which is the identification of two well-separated relaxation modes.

Results

The glass temperature of our polymer equals 97 °C, as determined by DSC analysis at a cooling rate of 10 °C min^{-1}. Figure 1 shows a fraction of the photon correlation function at temperature $T_g \pm 0.5$ °C. The rapid initial and slow decay at large times indicate that a simple exponential function cannot describe our results. The complete correlation function was constructed at four temperatures in the glass transition range. Overlapping data from runs using five or six different sampling increments are matched by a linear least-squares procedure with typical correlation coefficients of 99%. The results, normalized to unity at $t = 0$, are shown in Figure 2. The representation of the data according to eq 6 is seen in Figure 3. Evidently the correlation functions cannot be completely fitted by a single Williams–Watts expression, and in fact, two well-separated relaxation modes are apparent at each temperature. The characteristic parameters, β, τ_0, $\langle\tau\rangle$, and activation energy, E_a, for each mode as well as the fractional amplitude are listed in Table I.

Discussion

The most important conclusion of our experiments is the clear demonstration of two well-separated relaxation

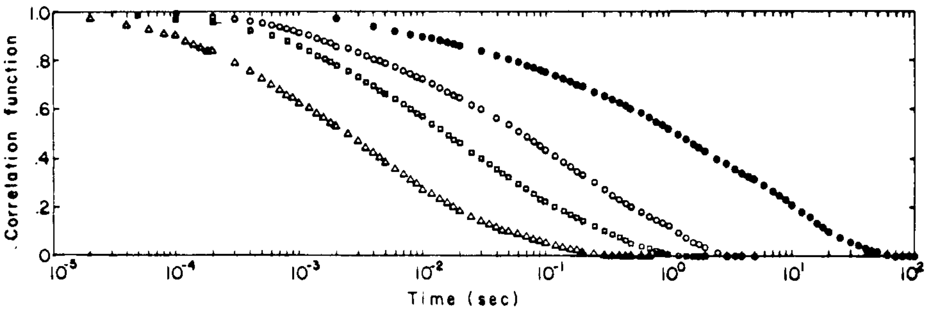

Figure 2. Composite photon correlation function $\phi^2(t)$ of light scattered at $\theta = 90°$ by atactic polystyene: (△) $T = 111.5$ °C; (□) $T = 107.0$ °C; (○) $T = 102.8$ °C; (●) $T = 96.7$ °C.

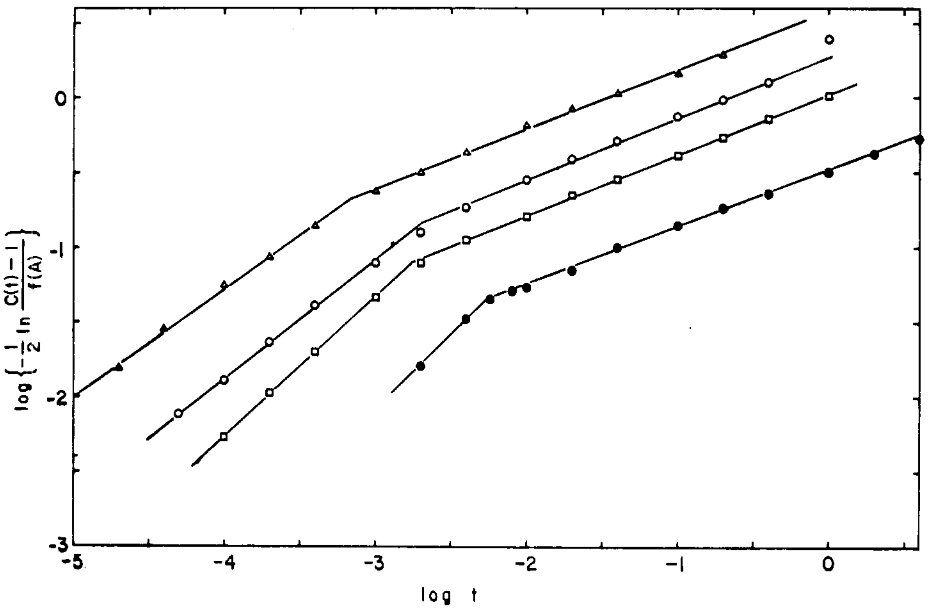

Figure 3. Plot of photon correlation data in the form $\log\{-^1/_2 \ln([C(t) - 1]/f(A))\}$ vs. $\log t$. The break in the linear slope of this plot indicates the presence of two relaxation modes: (△) $T = 111.5$ °C; (○) $T = 107.0$ °C; (□) $T = 102.8$ °C; (●) $T = 96.7$ °C.

modes in the correlation function of light scattered by polystyrene in the glass transition range. The characteristic frequencies f_c computed from

$$f_c = 1/(2\pi\langle\tau\rangle) \qquad (8)$$

are exhibited in Figure 4 together with points derived from $\langle\tau\rangle$ values determined in the depolarized light-scattering experiments of Patterson et al.[11] For purposes of comparison orientation lines m and d have been drawn, summarizing dynamic mechanical and dielectric information in the literature, respectively.[15,16] A point due to Stadnicki et al.[17] has been added. For reasons of clarity no other data points from mechanical experimentation are explicitly shown. The slow mode seen in our experiments comprises about 95% of the total detected intensity, and its amplitude appears to be slightly temperature dependent. The characteristic parameters are experimentally indistinguishable from those of the depolarized light-scattering process.[11] We may conclude that this particular mode or one or more slow modes with similar characteristics also contributes significantly to the isotropic scattering. In the glass-transition process then, the absolute magnitude of $\langle\tau_1\rangle$, determined by photon correlation spectroscopy, appears to be in accord with the dynamic mechanical result, thus emphasizing the difference between the latter and dielectric observations. Generally speaking, this difference would be consistent with a multistep process of widely different activation entropies but comparable enthalpies with some of these steps inactive in the mechanical or light scattering experiment.

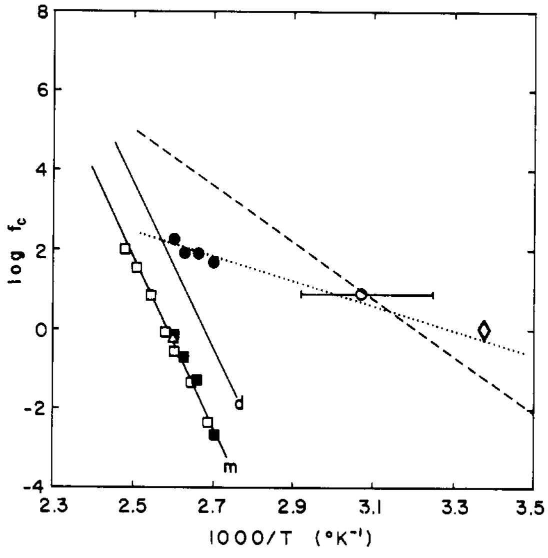

Figure 4. Relaxation frequency diagram for α and β modes of polystyrene: Line m, mechanical[15]; line d, dielectric data for α process; △, ref 17; □, ref 11; ■, this work. Dashed line, mechanical;[15,16] ○, ref 18; ◇, ref 19; ●, this work.

The fast decay is quite distinct with a β value indicative within experimental error of a single exponential term. Again two lines are seen in Figure 4. One accounts for mechanical literature data,[15,16] and the other is derived from our at present admittedly limited observations. The latter do, however, appear to be reasonably consistent with (averaged) mechanical observations by Schmieder and Wolf[18] and a measurement of Gillham.[19] Whereas the high apparent activation energy, $E_{a_1} \gtrsim 100$ kcal/mol, is characteristic of a glass-transition process, our value of $E_{a_2} \simeq$ 15 kcal/mol corresponds closely to expectation for a β relaxation. We recall a correlation by Heijboer[20] involving the activation enthalpy of a β process in kcal/mol, namely

$$E_a = 0.06T_\beta$$

to be applied at 1 Hz. Compressibility measurements of Quach and Simha[21] yield $T_\beta = 260$ K and thus $E_a \simeq 16$ kcal/mol. The second line drawn corresponds to $E_a \simeq 32$ kcal/mol. Boyer[22] notes a similar value for the crazing process in polystyrene and suggests a stress-induced additional process, superimposed on the intrinsic β relaxation. If this were indeed to be so, it would not arise in the present experimentation.

The results of this study indicate that photon correlation spectroscopy is a powerful tool in relaxation spectroscopy encompassing the glass transition as well as sub-glass relaxations. Further investigations of different polymer structures are obviously required, including both the depolarized and the isotropic (density fluctuations) contributions. A second important aspect is the comparative investigation of densified vs. "normal" glasses. It is established that the magnitudes of the densification vary widely[23] and one may expect substantial alterations in the dynamic and quasi-equilibrium characteristics of the density fluctuations.

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Autoacceleration of Free-Radical Polymerization. 4. Predissolved Polymer

K. A. High,[†] H. B. Lee,[‡] and D. T. Turner*

Dental Research Center, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514. *Received May 23, 1977*

ABSTRACT: The onset of autoacceleration of free-radical polymerization occurs when a critical concentration of polymer is formed from the monomer. This concentration can be predicted approximately from a theory which attributes the critical concentration to a condition of macromolecular close packing. The objective of the present work was to find whether quantitatively equivalent effects could be realized in the case where polymer was predissolved in monomer. Approximately, this was found when poly(methyl methacrylate) (PMMA) was predissolved in methyl methacrylate and then polymerization initiated by benzoyl peroxide. Similar experiments but with polystyrene in place of PMMA gave erratic results because of phase separation. Polystyrene predissolved in styrene was less effective in bringing on autoacceleration than in the case where polystyrene is formed in situ from monomer. It is tentatively suggested that this is because made-up solutions of polystyrene offer less resistance to the diffusion of polymer free radicals.

Rogovin and Tsaplina showed that the polymerization of methyl methacrylate is promoted by the presence of various dissolved polymers.[1] Independently, Trommsdorff, Köhle, and Lagally showed in more detail that the autoacceleration of polymerization of this monomer, initiated by benzoyl peroxide, was promoted by prior dissolution of either poly(methyl methacrylate) (PMMA) or cellulose tripropionate.[2]

The objective of the present work is to investigate whether the onset of autoacceleration caused by addition of polymer to a monomer conforms quantitatively to the same rules as were found to apply previously for polymer formed in situ during the polymerization reaction. This involves a comparison of the experimental dependence of the onset of autoacceleration, taking into account the concentration and molecular weight distribution of the

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[†] School of Medicine, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514.

[‡] Milton Roy Company, Sarasota, Florida 33578.