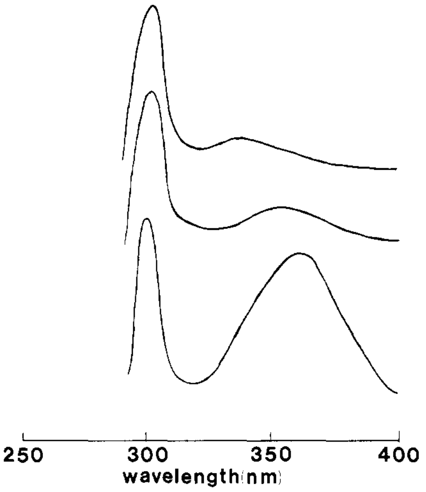

Figure 3. Fluorescence spectra of 4.0×10^{-3} N LaPSS in 0.50, 0.10, and 0.0010 N $LaCl_3$ from bottom to top, respectively.

are identical. This is also true for the divalent ions. It was interesting to note that the ability to form excimer depended on the hydrated radii of the counterions, with the largest hydrated ion, La^{3+}, least capable of excimer formation. For the counterions used here, their hydrated radii can be classified principally as tervalent > divalent > monovalent.[14] While it has been established that the most hydrated alkali metal ion binds least to the poly(styrenesulfonate) polyion,[15-17] it was at first surprising that the alkali metal ions did not bind to poly(styrenesulfonate) in the order generally found, i.e., $Li^+ < Na^+ < K^+ < Cs^+$. However, the type of counterion binding that favors excimer formation is specific inasmuch as it requires binding that causes plane-to-plane contact between the adjacent aromatic rings. Divalent ions in salt-free solutions yielded low excimer-to-monomer ratios than did the alkali metal ions. Each divalent metal ion can bind more readily to both sulfonate groups on adjacent aromatic rings than can alkali metal ions, thereby reducing the coplanarity between adjacent aromatic rings. This is probably due to the larger size of the hydrated divalent ions (Mg^{2+}, Ca^{2+}, and Sr^{2+} are 0.44, 0.42, and 0.42 nm, respectively[14]) as compared to the 0.25 nm between adjacent phenyl rings. Tervalent La^{3+} ion causes the largest reduction in coplanarity since it has the lowest excimer-to-monomer ratio in salt-free solution. It is interesting that the spectrum of a 4.0×10^{-3} N aqueous solution of poly[(vinylbenzyl)trimethylammonium chloride] showed only one band, with a maximum at 316 nm, and no excimer band because of the bulky ionic groups pendant from each phenyl ring.

The excimer-to-monomer ratios were found to be independent of simple salt concentration for LiPSS, NaPSS, CsPSS, and MgPSS. It appears that any change in the conformation of each of these polyelectrolytes due to a change in the ionic strength of the solution does not effect the short-range counterion-polyion interaction. For KPSS, CaPSS, SrPSS, and LaPSS, the excimer-to-monomer ratios were found to increase as the simple salt concentration was increased. This suggests that increased screening of the polyelectrolyte at the higher ionic strengths permits the adjacent phenyl groups to come closer together to form a tighter bond with these larger counterions. Hydrated counterion radii decrease as their concentration increases,[14] thereby, perhaps, facilitating excimer formation.

References and Notes

(1) Yanari, S. S.; Bovey, F. A.; Lumry, R. *Nature (London)* **1963**, *200*, 242.
(2) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.
(3) Morawetz, H. *Science (Washington, D.C.)* **1979**, *203*, 405.
(4) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(5) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.
(6) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 3249.
(7) Manning, G. S. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
(8) Manning, G. S. *Biophys. Chem.* **1977**, *7*, 95.
(9) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
(10) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443.
(11) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(12) Longworth, J. W.; Bovey, F. A. *Biopolymers* **1966**, *4*, 1115.
(13) Longworth, J. W. *Biopolymers* **1966**, *4*, 1131.
(14) Erdey-Gruz, T. "Transport Phenomena in Aqueous Solution"; Wiley: New York, 1974; Chapter 5.
(15) Caille, A.; Daoust, H. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 45*, 153.
(16) Tondre, C.; Zana, R. *J. Phys. Chem.* **1971**, *75*, 3367.
(17) Strauss, U. P.; Leung, Y. P. *J. Am. Chem. Soc.* **1965**, *87*, 1476.

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Separation of Two Relaxation Processes in Bulk Polymers Using Photon Correlation Spectroscopy at High Pressures

During the past 20 years the dynamic processes in amorphous polymers have been studied mainly by dielectric relaxation (DR).[1,2] Thus from the shapes of dielectric loss peaks two types of motion, known as α and β motions, have been characterized for a series of polymer melts. These two kinds of motion become indistinguishable and probably display a strong coupling at higher temperatures because of the different temperature dependence of the respective relaxation times τ. The different pressure dependence of τ has led to a fairly good resolution at most temperatures in the dielectric studies.[3-5] In general, the α mode in dielectric relaxation has been assigned mainly to collective motions involving several segments, while the assignment of the β mode to the dynamics of polar side groups seems to be questionable.

Recently, photon correlation spectroscopy has been applied to studies on bulk polymer dynamics with the hope of obtaining additional information, as the two methods monitor the polymer dynamics from a different viewpoint. So far the following polymers have been studied by dynamic light scattering: polystyrene (PS),[6-8] poly(methylphenylsiloxane) (PMPS),[9] poly(propylene glycol) (PPG),[10] and poly(ethyl methacrylate) (PEMA).[11] The experimental correlation functions for most of these polymers have been discussed in terms of local motions involving several chemical segments (α motion). The only exception was PMPS, for which the spectrum was shown to depend on the magnitude of the scattering vector **q**. For PS the observed dynamics have been assigned either to two relaxation processes (α, β)[6,8] or to a single process (α)[7], while the dielectric relaxation data of this polymer show both α and β relaxation processes. This uncertainty was not removed as yet because the light scattering experiments were carried out at constant pressure (1 bar). Thus the experiments were deprived of a valuable means of resolving the time scales. More recently, Patterson et al.[11] performed photon correlation measurements on PEMA and observed an exceptionally broad distribution of re-

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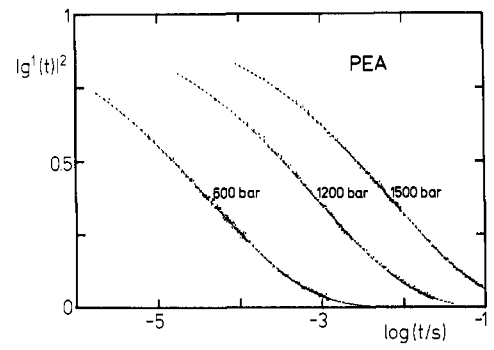

Figure 1. Composite correlation functions (dots) of PEA at 16.5 °C for three different pressures. The solid lines represent least-squares fits to the Williams–Watts equation.

laxation times near the glass transition temperature (T_g). Although the apparently small value of the distribution parameter β is an indication for the existence of more than one process, no separation could be obtained by changing the temperature only. In previous light scattering investigations the photon correlation spectra have been measured as a function of temperature at 1 bar. On the other hand, earlier DR measurements on bulk polymers have shown that two relaxation processes can be resolved by applying high pressures. In the case of PEA only one relaxation exhibiting a strong pressure dependence and a large apparent activation energy has been reported above the glass point T_g.[12] In contrast to this, from the loss peaks of PEMA, two discrete relaxations (α, β) have been resolved by applying high pressure.[3,4]

In order to obtain more detailed information about the nature of the two processes, we carried out a photon correlation spectroscopic study under pressure up to 2000 bar on PEA [poly(ethyl acrylate)] and PEMA. The two polymers were prepared by thermal polymerization of their freshly distilled monomers to remove the inhibitor contamination and by addition of an initiator [0.1 wt % of 2,2′-azobis(isobutyronitrile)] and were left for 2 months at 90 °C. Great care was taken to obtain a high-conversion polymer. This was checked by the Raman spectra[13] and the magnitude of the Landau–Placzek intensity ratio. Photon correlation functions for polarized scattering at different temperatures (265–300 K for PEA and 350–395 K for PEMA) and pressures between 1 and 2000 bar were taken at a scattering angle of $\theta = 90°$ with an apparatus to be described elsewhere.[14] The single-clipped correlation function was measured with a 96-channel Malvern correlator. The measured intensity autocorrelation function has the form $G^{(2)}(t) = A[1 + b|g^{(1)}(t)|^2]$, where $g^{(1)}(t)$ is the normalized correlation function of the electric field, A is the base line, and b is a fitting parameter; t ($=I\Delta\tau$) is the delay time (with I and $\Delta\tau$ being the channel number and the incremental delay time per channel, respectively). Since here we deal with relatively broad distributions of relaxation times, overlapping correlation functions from runs with different $\Delta\tau$ (differing by a factor of 10 between successive runs) were measured and matched, resulting in an overall correlation function covering usually 5 orders of magnitude in the time domain.[10] We have chosen to fit the function $g^{(1)}(t)$ with the empirical Williams–Watts form (W–W) $g^{(1)}(t) = \exp[-(t/\tau_0)^\beta]$, where β ($0 < \beta \leq 1$) is a measure of the width of the distribution of the decay times and τ_0 is the primary relaxation time. The average relaxation time, $\bar{\tau}$, is computed as $\bar{\tau} = (\tau_0/\beta)\Gamma(\beta^{-1})$, with $\Gamma(\beta^{-1})$ being the gamma function.

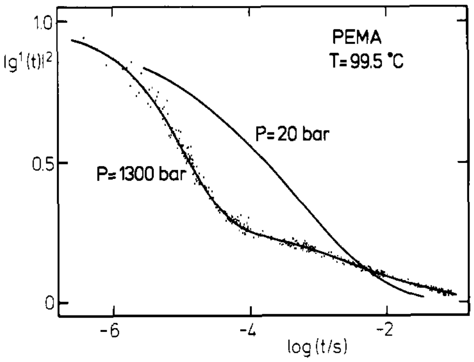

Figure 2. Composite correlation functions of PEMA at 99.5 °C for 20 and 1300 bar (dots) where the solid lines represent a least-squares fit to the single and the double Williams–Watts forms, respectively. The experimental points at 20 bar were omitted.

Figure 1 shows a semilog plot of the normalized correlation functions $|g^{(1)}(t)|^2$ for PEA at 16.5 °C at three different pressures (for the normalization procedure see ref 9 and 10). The solid line on the plot is the least-squares fit of the W–W equation to the composite correlation function. From this figure the large effect of the pressure on the mean relaxation time $\bar{\tau}$ is apparent. The distribution parameter β is found to be independent of pressure and temperature in the range used in this experiment and equal to 0.38. The coefficient $(\partial \log \bar{\tau}/\partial P)_T = 1.94 \times 10^{-3}$ bar^{-1} at 26 °C corresponds to the activation volume $\Delta V^* = 110$ cm^3/mol. This value is slightly temperature dependent and reflects the intermolecular interactions related to the conformational transitions as has been discussed previously.[10] The apparent activation energy $(\partial \ln \bar{\tau}/\partial(1/T))_P = 48$ kcal/mol is large, typical for an α process. The fit of the Fulcher–Vogel–Tamann equation, $\bar{\tau} \propto \exp[B/(T - T_0)]$, to the temperature dependence of the relaxation times $\bar{\tau}$ gives the high-temperature limiting activation energy $E_0 = RB = 2.8$ kcal/mol (R being the gas constant), which has been discussed in terms of conformational properties of the chain.[15,16] There is strong evidence that the observed relaxation in PEA is a single α process, in accord to the dielectric relaxation findings, and that it reflects local segmental motion at temperatures above T_g.

The effect of pressure on the composite correlation functions, which cover a wide time range of 5 orders of magnitude for PEMA, is shown in Figure 2. For the sake of simplicity Figure 2 shows correlation functions at 99.5 °C for two pressures only and the experimental points at 20 bar are omitted. While the correlation functions of PEMA at 20 bar are generally described in terms of a single process fitted with the W–W equation, it is expected that two processes might be resolved at some temperatures under higher pressures. The solid lines in Figure 2 represent the least-squares fit to a single and to a double W–W function for 20 and 1300 bar, respectively. The two processes in PEMA can be characterized, keeping in mind the following findings: (1) The fast process (β) is nearly independent of the pressure (1–1300 bar), in contrast to the slower (α) mode, which exhibits a strong pressure dependence similar to that of the α process observed in PEA (Figure 1). (2) The activation energy of the β mode at 1300 bar, a pressure where good resolution of the two processes is observed, is 15 kcal/mol, i.e., considerably smaller than for the α mode. (3) The value of the distribution parameter β for the β mode increases from 0.4 to 0.9 in the temperature range 80–120 °C. Alternatively, the value of

β for the α mode is virtually independent of temperature and equal to 0.35. The intensity of the β mode is about twice as large as that of the α mode in the well-resolved pressure–temperature region of the correlation function.

Thus photon correlation measurements at different pressures and temperatures have, for the first time to our knowledge, made possible the unambiguous resolution of the relaxation processes taking place in bulk polymers. Moreover, this method provides very useful information about the activation volume and energy.[14] The combination of light scattering and dielectric relaxation results will help us to shed some light on the molecular motions related to α and β modes in polymers, owing to the circumstance that each of the two methods leads to the correlation function of a different molecular property. This complementary aspect of the two techniques has proved extremely valuable in assigning definite modes to a particular relaxation process.

The detailed description of the experimental procedures, the methods of data fitting as well as the complete set of experimental results, and a more extensive discussion will be published elsewhere.[14]

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References and Notes

(1) McCrum, N. G.; Read, B. E.; Williams, G., Eds. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: New York, 1967.
(2) Karasz, F. E., Ed. "Dielectric Properties of Polymers"; Plenum Press: New York, 1972.
(3) Williams, G. *Trans. Faraday Soc.* **1966**, *62*, 2091.
(4) Sasabe, H.; Saite, S. *J. Polym. Sci., Part A-2* **1968**, *6*, 1401.
(5) Ishida, Y. *J. Polym. Sci., Part A-2* **1969**, *7*, 1835.
(6) Lee, H.; Jamieson, A. M.; Simha, R. *Macromolecules* **1979**, *12*, 329.
(7) Lindsey, C. P.; Patterson, G. D.; Stevens, J. R *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1547.
(8) Lee, H.; Jamieson, A. M.; Simha, R. *Colloid Polym. Sci.* **1980**, *258*, 545.
(9) Fytas, G.; Dorfmüller, Th.; Lin, Y.-H.; Chu, B. *Macromolecules* **1981**, *14*, 1088.
(10) Wang, C. H.; Fytas, G.; Lilge, D.; Dorfmüller, Th. *Macromolecules* **1981**, *14*, 1363.
(11) Patterson, G. D.; Stevens, J. R.; Lindsey, C. P. *J. Macromol. Sci., Phys.* 1981, *B18*, 641.
(12) Williams, G.; Watts, D. C. *NMR Basic Princ. Prog.* **1981**, *4*, 271–85.
(13) Chu, B.; Fytas, G.; Zalczer, G. *Macromolecules* **1981**, *14*, 398.
(14) Fytas, G.; Patkowski, A.; Meier, G.; Dorfmüller Th., to be published.
(15) Miller, A. A. *Macromolecules* **1978**, *11*, 859.
(16) Miller, A. A. *Polymer* **1979**, 20, 927.

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