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References and Notes

(1) (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(2) (a) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics*, in press.
(3) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.
(4) (a) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C. *Polym. Commun.* **1989**, *30*, 258. (b) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J., submitted for publication.
(5) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.
(6) (a) These catalysts have also been used to polymerize acetylene[6b] and benzvalene.[6c] (b) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004. (c) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 4413.
(7) Schrock, R. R.; Yap, K. B.; Yang, D. C.; Sitzmann, H.; Sita, L. R.; Bazan, G. *Macromolecules* **1989**, *22*, 3191.
(8) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; Davis, W. M.; O'Regan, M.; Schofield, M. H., submitted.
(9) ^{1}H NMR δ 12.00 (d, 1, J = 9.5 Hz, H_α), 7.92 (ddq, 1, J = 14.9, 9.5, 1.8 Hz, H_β), 4.77 (dq, 1, J = 14.9, 7.0 Hz, H_γ), 4.10 (sept, 2, J = 6.9 Hz, C*H*Me_2). Other resonances are obscured by resonances for polynorbornene.
(10) ^{1}H NMR (C_6D_6) δ 12.09 (s, 1, C*H*Ph), 4.02 (sept, 2, C*H*Me_2), 1.33 (s, 18, CMe_3), 1.23 (d, 12, CHMe_2), 7.0–7.2 (overlapping multiplets, aryl hydrogen atoms); ^{13}C NMR (C_6D_6) δ 247.8 (d, J_{CH} = 125.1 Hz, *C*HPh).
(11) Preliminary experiments indicate that *p*-methoxystyrene is an effective chain-transfer reagent. Treatment of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with 100 equiv of norbornene (10-min reaction time), then 20 equiv of *p*-methoxystyrene (30 min), and finally 200 equiv of norbornene (10-min reaction time) gave a 100-mer and a 200-mer with a PDI (both peaks together) of 1.17. A pulsing experiment involving addition of 5 portions of 100 equiv of norbornene in the presence of 25 equiv of *p*-methoxystyrene gave a 100-mer with PDI = 1.10.
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Registry No. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, 108969-04-6; *trans*-1,3-pentadiene, 2004-70-8; norbornene (homopolymer), 25038-76-0; styrene, 100-42-5; 2,3-bis(trifluoromethyl)norbornadiene (homopolymer), 72920-56-0.

Monitoring the Molecular Scale Effects of Physical Aging in Polymer Glasses with Fluorescence Probes

Physical aging is described as the gradual approach toward equilibrium of a nonequilibrium amorphous solid below T_g[1] and has been found to affect many properties of or processes in amorphous polymers: volume recovery,[1-4] enthalpy relaxation,[5] dielectric relaxation,[6] tensile modulus and stress relaxation,[7] yield stress,[8] positron annihilation,[9] neutron scattering,[10] X-ray scattering,[11,12] permeation,[13,14] electrical conductivity,[15] and the behavior of spectroscopic labels and probe molecules (electron spin resonance[16] and photochromic[17-19]). Only recently have the effects of physical aging on polymers been studied with fluorescence techniques.[19-21]

Loutfy et al.[22] demonstrated that the fluorescence quantum yields, intensities, and lifetimes of (dialkylamino)benzylidenemalononitriles (DAABMN) are sensitive to viscosity changes in low-viscosity solvents[22c] and follow a WLF free volume relation in high-viscosity media.[22c,g] Sensitivity to glass transitions of polymeric systems was also demonstrated, further suggesting a sensitivity to free volume and mobility.[22b,d,g] These charge transfer probes are viscosity sensitive through rotational nonradiative decay mechanisms from the singlet excited state. Three mechanisms have been identified for these probes: rotation of the donor group,[22,23] rotation of the acceptor group,[22,23] and isomerization around the double bond.[23-25] A decrease in these rotational abilities increases the probability of radiative decay; hence, the fluorescence quantum yield, intensity, and lifetime increase. Therefore, the fluorescence intensity increases with an increase in local viscosity or a decrease in the local mobility or free volume.

We have found that DAABMN probes have the sensitivity to monitor the changes that occur in polystyrene and poly(methyl methacrylate) glasses during physical aging and report the preliminary results in this paper.

Experimental Section. Polystyrene (PS; nominal MW = 575 000; $M_w/M_n \le 1.06$) and poly(methyl methacrylate) (PMMA; nominal MW = 265 600; $M_w/M_n \le 1.15$) were used as received from Pressure Chemical. The fluorescence probes used were 4-(diethylamino)benzylidenemalononitrile (DEABMN) and 4-(dimethylamino)benzylidenemalononitrile (DMABMN) (from Molecular Probes).

Films doped with fluorescent probe were cast from 7 wt % polymer solutions in dichloromethane (Aldrich, spectrophotometric grade) onto 2 in. × 2 in. × 1/16 in. quartz slides. After they were dried at ambient temperature and pressure for 24 h, the PS films were dried 1 day under vacuum at 25 °C and an additional 2 days under vacuum at 60 °C to remove residual solvent. PMMA films were dried at ambient temperature and pressure for 1 week before being placed under vacuum at 60 °C for 2 days. PMMA films required additional time at ambient conditions to avoid bubbling during vacuum drying. Dry films contained less than 0.01 wt % probe and were less than 150 μm thick.

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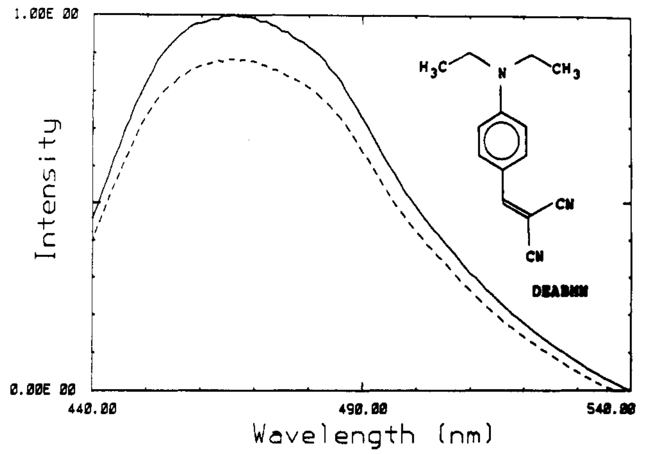

Figure 1. Fluorescence emission spectra and structure of DEABMN in PS after physical aging at 90 °C for 5 min (dashed line) and 6 h (solid line).

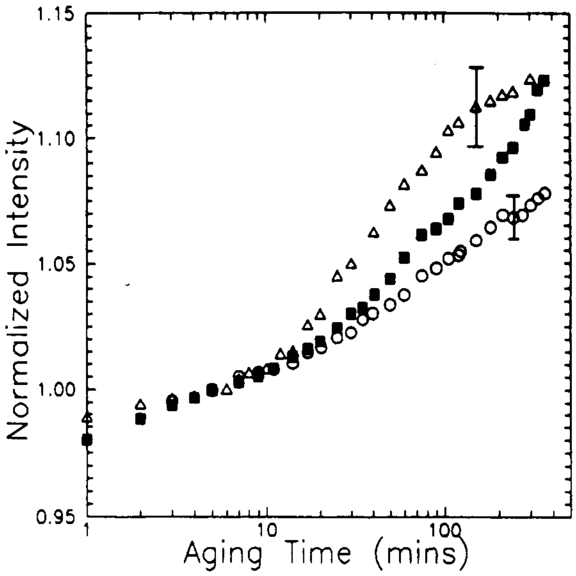

Figure 2. Normalized fluorescence intensity of DEABMN in PS versus the logarithm of aging time at 30 °C (○), 60 °C (■), and 90 °C (△). Intensities were measured at 464–466 nm, the wavelength range of maximum emission for DEABMN in PS. Errors are the size of the symbols before 100 min. After 100 min, the errors are given by the error bars. Error bars were calculated from results of at least three experiments.

The thermal history of each film was carefully erased by heating at 20 °C above T_g for 1 h in an oven immediately before performing aging experiments. Films were removed from the oven and quickly placed into a specially designed temperature cell, which quenched the sample to the desired temperature in less than 3 min and allowed fluorescence spectra to be taken while the film was maintained at the aging temperature during the entire experiment. Total time between removal from the oven and the ability to record the first spectrum was less than 1 min. Steady-state fluorescence emission spectra of the doped films were recorded at the aging temperature with a SPEX Fluorolog-2 DM1B spectrofluorimeter in a front-face geometry with 2.5-mm excitation and emission slits (band-pass of 9.0 nm). Excitation wavelengths were 420 nm for DEABMN and 432 nm for DMABMN in both PS and PMMA. Changes in the fluorescence intensity caused by aging were recorded at various intervals of aging time.

Results and Discussion. Figure 1 contains the chemical structure and fluorescence emission spectrum of DEABMN in PS, which is similar to other DAABMN probes reported by Loutfy.[22] Figure 1 demonstrates that 6 h of aging in PS at 90 °C results in an 11% increase in the DEABMN emission at the wavelength of maximum intensity but not in a change in the shape of the peak.[26] This increase in intensity may be interpreted as resulting from the loss of mobility or free volume in the polymer matrix, which impedes the nonradiative decay motions of the excited probe. (See ref 26.)

Figure 2 illustrates the intensity at the emission maximum for DEABMN in PS as a function of the logarithm of aging time at several aging temperatures. All curves have been normalized to an intensity of 1 at 5 min of aging time to eliminate intensity differences between films due to different aging temperatures and probe concentrations. Figure 2 contains many interesting features. The overall slope of a curve increases with increasing aging temperature. When our interpretation of the increase in fluorescence intensity is applied for the aging times investigated, the PS glass ages at an increasingly faster rate as the aging temperature is increased toward T_g (near 100 °C for high molecular weight PS). These curves represent the change in local mobility (or free volume) around the probe relative to the amount of mobility present initially after the temperature quench above T_g. Such a trend may be expected since mobility and free volume in polymeric glasses increase as the temperature approaches T_g.

Upon close inspection at different aging temperatures, we found that the changes in fluorescence intensity are not linear with the logarithm of aging time as reported earlier.[20] Instead, the rate of increase in fluorescence intensity with respect to logarithmic aging time is considerably smaller at aging times less than 20 min than for longer aging times. Greiner and Schwarzl have reported an "initial plateau"[4a] in specific volume relaxations for PS undergoing physical aging. (They found that at short aging times the specific volume hardly changed.) However, while the apparently reduced response of the fluorescence probes at short aging times could be interpreted as being related to this initial plateau, it must be noted that the relevant "short" time frames for the two experiments differ significantly at lower aging temperature. Furthermore, this initial plateau in specific volume measurements was not reported in similar dilatometric studies of polystyrene by Adachi and Kotaka[3] and in a later investigation by Greiner and Schwarzl.[4b] Studies are currently being conducted to determine the cause and significance of the shift in slope of the fluorescence intensity versus logarithmic aging time for these and other mobility-sensitive fluorescence probes. Referring to the 90 °C curve in Figure 2, the DEABMN fluorescence intensity changes relatively little over the 100–300-min aging range and may be approaching a plateau. Assuming DEABMN responds to the local mobility, this behavior suggests two possibilities. One interpretation is that the local environment around the probe may have lost the mobility or free volume to allow the nonradiative decay motions to take place. A plateau resulting from completely rigid environments around the probes is unlikely in view of the evidence that photochromic probes (which probably sense much larger environments than these fluorescence probes) are able to isomerize after 100 h of aging at 70 °C in PS.[19] A second more interesting possibility is that the environments sensed by DEABMN may be approaching an equilibrium. If this is the case, then DEABMN may not be sensing the bulk specific volume equilibrium, which occurs between 12 days[3] and 5 mo[4] at 90 °C. The fluorescence intensity of DEABMN may

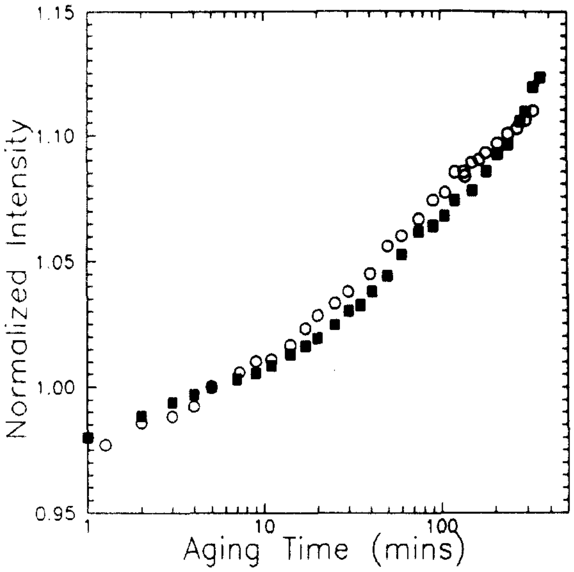

Figure 3. Normalized fluorescence intensity versus the logarithm of aging time at 60 °C for DEABMN in PS (■) and DMABMN in PMMA (○).

be responding to a small fraction of a distribution of environments that, as a sum, are responsible for bulk specific volume relaxations. Further studies employing probes that require different volumes to decay nonradiatively are needed to determine the degree to which these probes are sensing a distribution of environments in the polymer.

Changes in DMABMN fluorescence intensity yield the same physical aging dependence within experimental error as DEABMN for PS systems studied at 90 °C. This suggests replacing the ethyl groups in DEABMN with methyl groups results in little change in sensitivity to mobility in polystyrene and is not sufficient to sense different fractions of the distribution.

It is possible as well to compare physical aging effects measured by these probes as a function of polymer matrix. In PS and PMMA, the most noteworthy difference in the probe fluorescence behavior is in terms of the wavelength associated with the maximum fluorescence intensity. For DEABMN and DMABMN, the fluorescence maximum shifts by 6–9 nm, from 464–466 nm in PS to 472–473 nm in PMMA. This red shift in the more polar matrix is characteristic of these probes and has been observed in a number of solvents.[22] It is interesting to note that the relative increases in fluorescence intensity of DEABMN or DMABMN probes during 5–6 h of physical aging at 60 °C in PS and PMMA are strikingly similar, as shown in Figure 3. These results suggest that the different environments in PS and PMMA sensed by the probes age similarly under these conditions.

We have demonstrated that a fluorescence technique involving a very low concentration of viscosity-sensitive probes is able to monitor changes in glassy polymers during physical aging. Studies involving a variety of fluorescence probes that may exhibit sensitivity to different fractions of a distribution (not observed by DEABMN and DMABMN) and involving treatments besides physical aging that alter bulk relaxation behavior (e.g., plasticization, strains, and temperature jumps) are underway.

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References and Notes

(1) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, The Netherlands, 1978.
(2) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097.
(3) Adachi, K.; Kotaka, T. *Polym. J.* **1982**, *14*, 959.
(4) (a) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378. (b) Greiner, R.; Schwarzl, F. R. *Colloid Polym. Sci.* **1989**, *267*, 39.
(5) Marshall, A. S.; Petrie, S. E. B. *J. Appl. Phys.* **1975**, *46*, 4223.
(6) Matsuoka, S.; Williams, G.; Johnson, G. E.; Anderson, E. W.; Furukawa, T. *Macromolecules* **1985**, *18*, 2652.
(7) Cizmecioglu, M.; Fedors, R. F.; Hong, S. D.; Moacanin, J. *Polym. Eng. Sci.* **1981**, *21*, 940.
(8) Bauwens, J. C. *Plast. Rubber Process. Appl.* **1987**, *7*, 143.
(9) Kobayashi, Y.; Zheng, W.; Meyer, E. F.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1989**, *22*, 2302.
(10) Bubeck, R. A.; Yasar, H. Y.; Hammouda, B. H. *Polym. Commun.* **1989**, *30*, 25.
(11) Roe, R. J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428.
(12) Curro, J. J.; Roe, R. J. *Polymer* **1984**, *25*, 1424.
(13) Levita, G.; Smith, T. L. *Polym. Eng. Sci.* **1981**, *21*, 936.
(14) Coll, H.; Searles, C. G. *Polymer* **1988**, *29*, 1266.
(15) Munstedt, H. *Polymer* **1988**, *29*, 296.
(16) (a) Tsay, F. D.; Hong, S. D.; Moacanin, J.; Gupta, A. *Bull. Am. Phys. Soc.* **1982**, *27*, 393. (b) Tsay, F. D.; Hong, S. D.; Moacanin, J.; Gupta, A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 763. (c) Tsay, F. D.; Gupta, A. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 855.
(17) Priest, W. J.; Sifain, M. M. *J. Polym. Sci., Part A-1* **1971**, *9*, 3161.
(18) (a) Sung, C. S. P.; Lamarre, L.; Chung, K. H. *Macromolecules* **1981**, *14*, 1839. (b) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729. (c) Sung, C. S. P.; Gould, I. R.; Turro, N. J. *Macromolecules* **1984**, *17*, 1447. (d) Yu, W. C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355.
(19) (a) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241. (b) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2951. (c) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 3490. (d) Royal, J. S.; Victor, J. G.; Torkelson, J. M., to be submitted for publication.
(20) The sensitivity of the fluorescence probes DEABMN and DMABMN to physical aging in PS was first reported by us at the March 1989 American Physical Society Meeting. Similar sensitivity for the fluorescence probe Auramine O in glassy polymers was reported by E. F. Meyer, A. Jamieson, and R. Simha at the same meeting.
(21) Meyer, E. F.; Jamieson, A. M.; Simha, R.; Palmen, J. H. M.; Booij, H. C.; Maurer, F. H. J. *Polymer* **1990**, *31*, 243.
(22) (a) Loutfy, R. O.; Law, K. Y. *J. Phys. Chem.* **1980**, *84*, 2803. (b) Loutfy, R. O. *Macromolecules* **1981**, *14*, 270. (c) Loutfy, R. O.; Arnold, B. A. *J. Phys. Chem.* **1982**, *86*, 4205. (d) Loutfy, R. O. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 825. (e) Loutfy, R. O.; Teegarden, D. M. *Macromolecules* **1983**, *16*, 452. (f) Loutfy, R. O. *Macromolecules* **1983**, *16*, 678. (g) Loutfy, R. O. *Pure Appl. Chem.* **1986**, *58*, 1239.
(23) Abdel-Mottaleb, M. S. A.; Loutfy, R. O.; Lapouyade, R. *J. Photochem. Photobiol. A* **1989**, *48*, 87.
(24) (a) Safarzadeh-Amiri, A. *Chem. Phys. Lett.* **1986**, *129* (3), 225. (b) Safarzadeh-Amiri, A. *Can. J. Chem.* **1984**, *62*, 1895. (c) Safarzadeh-Amiri, A. *Chem. Phys.* **1988**, *125*, 145.
(25) Organic Photochemistry Group, 3M Co., personal communication.
(26) Decreasing dynamic oxygen quenching is not a major contributor to the increase in fluorescence intensity with aging time. We performed experiments where a poly(vinyl acetate) film was subjected to 35 pump–purge cycles (pumped in a vacuum oven and purged with high-purity nitrogen gas) at 60 °C (25 °C above T_g) over 4 days. Results from aging experiments performed under N_2 were not different (within experimental error) from those obtained with films that were constantly exposed to air.
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