Registry No. Water, 7732-18-5; poly(bisphenol A diglycidyl ether), 25085-99-8.

References and Notes

(1) Browning, C. E. *Polym. Eng. Sci.* **1978,** *18,* 16.
(2) Illinger, J. L.; Schneider, N. S. In "Water in Polymers"; Rowland, S. P., Ed.; American Chemical Society, Washington, D.C., 1979; ACS Symp. Ser. No. 127.
(3) Morgan, R. J.; O'Neal, J. E. *Polym. Plast. Technol. Eng.* **1978,** *10,* 49.
(4) Banks, L.; Ellis, B. *Polym. Bull.* **1979,** *1,* 377.
(5) Moy, P.; Karasz, F. E. *Polym. Eng. Sci.* **1980,** *20,* 4.
(6) Miyayi, Z.; Tanaka, K. *Polymer* **1975,** *16,* 441.
(7) Tan, Y. Y.; Challa, G. *Polymer* **1976,** *17,* 739.
(8) Sung, Y. K.; Gregonis, D. E.; Russell, G. A.; Andrade, J. D. *Polymer* **1978,** *19,* 1362.
(9) Moy, P. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1980.
(10) ten Brinke, G.; Karasz, F. E.; Ellis, T. S. *Macromolecules* **1983,** *16,* 244.
(11) Lawing, D.; Fornes, R. E.; Gilbert, R. E.; Memory, J. D. *J. Appl. Phys.* **1981,** *52,* 5906.
(12) Fuller, R. T.; Fornes, R. E.; Memory, J. D. *J. Appl. Polym. Sci.* **1979,** *23,* 1871.
(13) Davis, J. H.; Jeffrey, K. R.; Bloom, M.; Valic, M. I.; Higgs, T. P. *Chem. Phys. Lett.* **1976,** *42,* 390.
(14) Blinc, R.; Rutar, V.; Seliger, J.; Slak, J.; Smolej, V. *Chem. Phys. Lett.* **1977,** *48,* 576.
(15) See, for example: Jelinski, L. W.; Sullivan, C. E.; Torchia, D. A. *Nature (London)* **1980,** *284,* 531. Hentschel, D.; Sillescu, H.; Spiess, H. *Macromolecules* **1981,** *14,* 1605. Huang, T. H.; Skarjune, R. P.; Wittebort, R. J.; Griffin, R. G.; Oldfield, E. *J. Am. Chem. Soc.* **1981,** *102,* 7377.
(16) Hentschel, R.; Spiess, H. W. *J. Magn. Reson.* **1979,** *35,* 157.
(17) Bloom, M.; Davis, J. H.; Valic, M. I. *Can. J. Phys.* **1980,** *58,* 1510.
(19) Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* **1981,** *42,* 381.
(19) Collignon, J.; Sillescu, H.; Spiess, H. W. *Colloid Polym. Sci.* **1981,** *295,* 220.
(20) Mehring, M. In *NMR: Basic Princ. Prog.* **1976,** *11.*
(21) Several broad-line proton NMR studies have been reported on epoxy-water systems.[3,4,11,12] The deuterium NMR approach used here has the advantages that D_2O can be observed selectively, without competing signals from the resin, and that the resultant line shape is straightforward to analyze.

Lynn W. Jelinski* and Joseph J. Dumais
Bell Laboratories
Murray Hill, New Jersey 07974

Ruth E. Stark
Department of Chemistry
Amherst College
Amherst, Massachusetts 01002

Thomas S. Ellis and Frank E. Karasz
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003

Received April 25, 1983

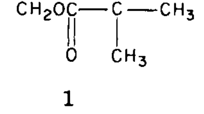
How Dense-Packed Are Collapsed Polymer Chains in Dilute Solution?

Ever since the concept of a Θ solvent was first presented,[1] it was recognized that below the Θ temperature a polymer molecule should suffer an important decrease in its mean dimensions. These decreased dimensions have been notoriously difficult to study. Most experiments fail because polymer molecules are simply not very soluble below $T = \Theta$. This means that appropriate experiments must examine kinetically metastable solutions, in which, because of the enormous dilution of the polymer molecules, the collapse transition would occur much faster than the aggregation and precipitation of macromolecules. Such transitions have been observed by light scattering on very high molecular weight polystyrene polymers,[2] where the high sensitivity of the light scattering technique for polymers of this high molecular weight allows one to carry out experiments in the ppb to ppm concentration range.

Fluorescence and phosphorescence techniques are potentially useful for examining the properties of polymer molecules at high dilution. One needs typically only 1×10^{-6} M concentration of chromophore to detect emission intensity with ease, and one can realistically work with solutions a factor of 10 more dilute. This means that experiments can be carried out at 1 ppm (weight fraction) of polymer, particularly if the polymer contains more than one chromophore per chain.

In this paper we present our observations on the phosphorescence intensity of naphthalene groups attached covalently to a polymer chain. These observations are compared to those on a small molecule containing the same chromophore. In dilute solution, at room temperature or in rigid low-temperature matrices, both show similar luminescence properties. At low temperatures, near the melting point of the solvent, where the solvent is presumably a very poor (sub-Θ) solvent for the polymer, we see indications of collapse of single chains. Our results suggest that these polymer molecules form configurations so compact that the diffusion of oxygen within the coil is retarded by ca. 10 orders of magnitude over its value at room temperature in the same solvent.

Experimental Section. The experiments reported here involve a graft copolymer of poly(methyl methacrylate) (PMMA) and polyisobutylene in which the PMMA blocks contain 10 mol % naphthalene groups distributed randomly along their length. The naphthalene groups were introduced in the form of 1-naphthylmethyl methacrylate during the synthesis of the polymer. This material is reasonably polydisperse. Most of the polymers have apparent molecular weights (by GPC) in the range 20 000–80 000. The isobutylene content by NMR is approximately 10 mol %. These materials were prepared as nonaqueous dispersions of 2-μm particles in isooctane. Their preparation and characterization have been described elsewhere.[3] In these experiments, the polymer was dissolved in ethyl acetate at a weight concentration of ca. 10 ppm, which corresponds to a naphthalene (N) concentration of 7×10^{-6} M. The solutions were placed in 3-mm-i.d. quartz tubes for phosphorescence analysis. The N groups were excited with light at 280 nm. Some of the tubes were outgassed by bubbling argon gas into the solutions for 30 s to 1 min. Emission spectra were compared to that of the model compound 1-naphthylmethyl pivalate (1).



1

Results and Discussion. When solutions of the polymer or of 1 in ethyl acetate were immersed in liquid nitrogen, essentially transparent glassy matrices were formed. In these, both fluorescence and phosphoresce from N could be observed. At room temperature, only N fluorescence was observed: the presence of oxygen or other trace impurities at the 10^{-8}–10^{-9} M level effectively quenched the N triplets before they could emit.

In Figure 1a we show what happens to the phosphorescence intensity of the model compound 1 as a frozen

0024-9297/83/2216-1021$01.50/0

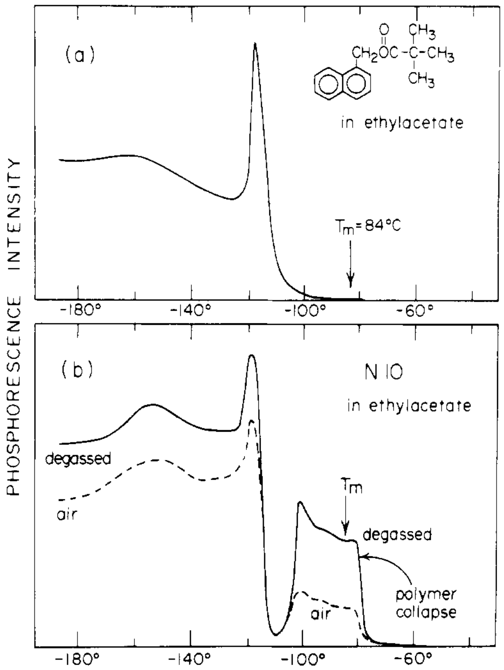


Figure 1. Naphthalene phosphorescence intensity as a function of temperature for dilute solutions in ethyl acetate that were rapidly cooled to liquid nitrogen temperature and then allowed to warm: (a) 1-naphthylmethyl pivalate in degassed solution; (b) N10 copolymer with the naphthalene groups covalently attached to the polymer chain. The dashed line refers to an air-saturated solution; the solid line refers to a degassed solution.

solution of it in ethyl acetate is allowed to warm up from liquid nitrogen temperature. As the sample warms, the phosphorescence intensity passes through a modest maximum at −160 °C, decreases somewhat, and then peaks sharply at −120 °C. By −100 °C the emission is barely perceptible, and by the ethyl acetate melting point, −84 °C, it can no longer be detected.

When the polymer containing N groups is examined in the same way, Figure 1b, similar features are seen in the temperature dependence of the phosphorescence intensity below −110 °C. Above −110 °C, a rather remarkable feature is observed. The phosphorescence intensity grows back in, peaks at −100 °C, decays slowly until the temperature reaches −78 °C (above the melting point of ethyl acetate), and then disappears. In air-saturated solutions, similar behavior is observed, but the overall intensities are reduced.

There are two sets of observations that need to be explained. First the phosphorescence intensity fluctuations between −160 and −110 °C, for both the model compound 1 and the polymer-bound naphthalene groups, are unexpected. There is nothing unique about phosphorescence from naphthalene chromophores. All indications point to relaxation processes within the solvent as being responsible for these intensity fluctuations seen in Figure 1b. We *rationalize* these observations as follows, taking care to emphasize that other factors also may be operative.

Phosphorescence from simple polycyclic aromatic molecules normally can be observed only when impurity diffusion is suppressed. In fluid solution this means that impurity levels of even 10^{-8} M make detection of residual unquenched phosphorescence nearly impossible; and in very viscous solvents, 10^{-5}–10^{-6} M impurities have the same effect. Consequently, one normally measures phosphorescence in rigid low-temperature organic matrices, in crystalline hosts, or in glassy polymer matrices (e.g., PMMA) at room temperature. Since temperature itself has relatively little effect on the phosphorescence of 1, its phosphorescence intensity fluctuations between −160 and −110 °C in ethyl acetate must originate in factors affecting the accessibility of trace impurities to the excited molecules during the 2-s triplet lifetimes.

At the lowest temperatures only static quenching occurs. The solvent is trapped in a nonequilibrium glassy state where motion of the solvent molecules is inhibited. We attribute the rising portion of the peak at −120 °C to the onset of solvent molecule motion, leading to the formation of microcrystals that entrap chromophores. This presumably minimizes static quenching and further retards diffusive quenching by residual oxygen. Above −120 °C, crystal growth in the solvent expels chromophores. Both static and diffusive quenching occur, the latter becoming dominant and ultimately supressing phosphorescence entirely.

Even more remarkable than the phosphorescence intensity changes below −110 °C is the observation of renewed phosphorescence from the polymer-bound N groups, between −100 and −78 °C, *even in the presence of air.* We believe there is a unique explanation of this phenomenon, associated with polymer collapse protecting some of the chromophores from impurity quenching.

This kind of observation has precedence in the observation by Galley and co-workers[4] of phosphorescence from tryptophan groups in liver alcohol dehydrogenase in water solution at room temperature. In the protein system, one can distinguish tryptophans at the surface from those buried in the interior. In a frozen matrix both types phosphoresce. In fluid solution, tryptophan groups near the surface of the protein are susceptible to impurity quenching. The phosphorescence observed emanates only from those interior chromophores, where, one argues, the dense-packed protein structure protects them from oxygen quenching.

Applying this point of view to our observations of the naphthalene-containing polymer in the temperature range −78 to −105 °C, we conclude that the polymer has collapsed dimensionally and that the packing density within the collapsed coil is sufficient to suppress contact of the N groups with oxygen in the solvent. The polyisobutylene segments of the graft copolymer may contribute to this effect. Aggregation under these conditions of low polymer concentration and high solvent viscosity is considered to be unlikely. The rate of phosphorescence quenching is proportional to the product of the diffusion coefficient of oxygen and its concentration in the polymer coil. This concentration is unknown. We note, however, that in the air-saturated solution, the phosphorescence intensity is approximately half that in the outgassed sample. If we assume that quenching involves diffusion of oxygen molecules over a distance of ca. 100 Å in 1 s, we calculate an effective diffusion coefficient of 10^{-16} cm^2 s^{-1}. This value is more than 10 orders of magnitude slower than the diffusion of oxygen in ethyl acetate solution at room temperature.

Acknowledgment. We thank NSERC Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. The manuscript was written while M.A.W. was a visiting scientist at the IBM Research Laboratories, San Jose, CA. He wishes to express his appreciation to Drs. B. A. Smith and J. Economy for their kind hospitality.

Note Added in Proof: Turro and co-workers[5] recently reported that binding a naphthalene derivative to a cyclodextrin afforded sufficient protection against oxygen quenching that phosphorescence in aqueous solution could be observed.

Registry No. Isobutylene–methyl methacrylate–1-naphthylmethyl methacrylate copolymer, 84802-24-4; 1-naphthylmethyl pivalate, 72681-59-5; oxygen, 7782-44-7.

References and Notes

(1) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.

(2) (a) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981,** *32,* 433–451. (b) Swislow, G.; Sun, S. T.; Nishio, I.; Tanaka, T. *Phys. Rev. Lett.* **1980,** *44,* 796.

(3) (a) Pekcan, O.; Winnik, M. A.; Egan, L.; Croucher, M. D. *Macromolecules* **1983,** *16,* 699–702. (b) Pekcan, O.; Winnik, M. A.; Croucher, M. D. *J. Colloid Interface Sci.,* in press.

(4) Saviotti, M. L.; Galley, W. C. *Proc. Natl. Acad. Sci. U.S.A.* **1974,** *71,* 4154–4159.

(5) Turro, N. J.; Cox, G. S.; Li, X. *Photochem. Photobiol.* **1983,** *37,* 149–153.

(6) On leave from the Department of Physics, Hacettepe University, Ankara, Turkey.

Mitchell A. Winnik* and Onder Pekcan[6]

Lash Miller Laboratories, Department of Chemistry, and
Erindale College, University of Toronto
Toronto, Ontario L5L 1C6, Canada

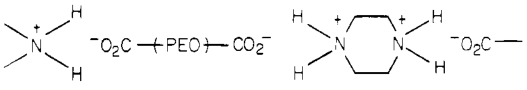
Received December 28, 1982

Novel Polycondensations via Poly(oxyethylene) Diglycolic Acid Diamine Salts

Poly(oxyethylene) diglycolic acid[1] ("PEO-acid") (1) is a new telechelic derivative of poly(oxyethylene). It is characterized by two terminal carboxyl groups quantitatively introduced by the selective oxidation (Pd–Pt catalyst) of the terminal methylol groups on poly(ethylene glycol) (PEG)[2] and can be prepared with narrow molecular weight distribution with a wide variety of $\bar{M}_n$. We are now studying various chemical syntheses and polymerizations based on PEO-acid.

This first report discloses preparations of novel 1:1 salts of PEO-acids with piperazine (**2a**) and with 1,6-diaminohexane (**2b**) (Scheme I). In the present study, PEO-acids with relatively low molecular weight ($\bar{M}_n$ = 400 (**1a**[3]) and $\bar{M}_n$ = 1000 (**1b**[4])) were utilized. The piperazine salts of **1** were isolated as crystalline solids, while the diaminoxhexane salts were amorphous waxes. These salts are analogues of the well-known "nylon 6,6 salt",[5] formed between adipic acid and **2b**. They, like the "nylon salt", can be converted to high polymer by the removal of water at elevated temperature as shown in Scheme I.

Thus, a mixture of 4.0 mmol each of purified **1a** and **2a** was maintained at 50 °C for 1 h with stirring under a nitrogen atmosphere. A glassy material was produced in quantitative yield and was recrystallized from an 80/20 chloroform–diethyl ether mixture to afford a white crystalline product. After filtration and drying in vacuo **3a-1** was isolated in 45% yield: $\eta_{sp}/C = 0.028^3$ (5.0 g/L in H_2O at 30 °C); ^1H NMR (D_2O) δ 3.53 (s, NCH_2CH_2N, 8 H), 3.72 (s, OCH_2CH_2O, 26.8 H), 3.97 (s, OCH_2CO_2, 4 H); IR (KBr) 3400 (ν_{O-H}), 3250, 3020 (ν_{N^+-H}), 2930 (CH_2), 1600, 1400 ($\nu_{C=O}$ of CO_2^-), 1100 (ν_{C-O}) cm^{-1}. Anal. Calcd for **3a-1**·$[H_2O]_{1.0}$ (n = 6.7): C, 47.89; H, 8.51; N, 5.25. Found (very hygroscopic): C, 47.53; H, 8.34; N, 5.50. This product melted at 53–56 °C to a liquid that still transmitted polarized light weakly. This finding suggests the existence of a molecular orientation (somewhat liquid crystalline) that may result from intermolecular salt formation (structure 5). The light transmission sharply disappeared at 80 °C and could be recovered quite reversibly at this temperature unless the samples were heated over 100 °C, around which irreversible polymerization occurred. These results were supported by the DTA analysis shown in Figure 1a. The broad endothermic peak at 55 °C and the complicated exothermic ones over 100 °C correspond, respectively, to the melting point and to the initiation of the condensation reaction (vide infra). The sharp shoulder observed at 80 °C corresponds to the disappearance of the mesomorphic phase.



5

The salt **3a-2** was also obtained as a crystalline solid:[6] mp 40 °C; $\eta_{sp}/C = 0.032^4$ (5.0 g/L in H_2O). Anal. Calcd for **3a-2**·$[H_2O]_{2.0}$ (n = 20.3): C, 50.74; H, 8.87; N, 2.43. Found (very hygroscopic): C, 50.85; H, 9.16; N, 2.38. However, the isolated yield was as low as 20% because of difficulty in recrystallization. This compound melted at 40 °C to a liquid that allowed little transmission of polarized light and began to decompose around 150 °C. The mesomorphic state found in **3a-1** was not observed in **3a-2** by DTA (Figure 1b). As for the uncrystallized parts of both **3a-1** and **3a-2**, they were also obtained as solid materials on drying and found to be structurally identical with the crystalline products by spectroscopy.[7]

The reactions of **2b** with **1a** and with **1b** were carried out in a similar manner. In these cases, the products obtained were washed twice with diethyl ether and dried in vacuo and were isolated in 95% yield as an amorphous waxy solid[8] that did not transmit polarized light.

All the above salts were allowed to polymerize by thermal condensation. Typically, the salt **3a-1** (1.0 g) was placed in a glass tube, heated under a stream of nitrogen as the temperature was raised slowly to 200 °C in 3 h, and then maintained at 200 °C for another 3 h in vacuo to complete the elimination of water. A white waxy polymer was obtained in quantitative yield and was used without further purification. The structure **4a-1** was confirmed by the following data: ^1H NMR ($CDCl_3$) δ 3.60 (s, NCH_2CH_2N, 8 H), 3.65 (s, OCH_2CH_2O, 18.8 H), 3.70 (s, $C(O)CH_2OCH_2CH_2O$, 8 H), 4.24 (s, $C(O)CH_2O$, 4 H); IR (KBr) 2880 (CH_2), 1640 ($\nu_{C=O}$ of amide), 1450, 1105 (ν_{C-O}) cm^{-1}, etc. Anal. Calcd for **4a-1** (n = 6.7): C, 53.60; H, 8.16; N, 5.85. Found (very hygroscopic): C, 53.21; H, 8.09; N, 5.66. Polymerizations of the other salts were carried out similarly. The results are summarized in Table I. When the mixture of **1** and **2** was directly heated without isolating the salt, the molecular weight of the product was much lower.

The salt **3** is conveniently utilized for the copolycondensation with "nylon 6,6 salt". For example, a 1:1 mixture of **3b-1** with the latter (1.0 g each) was allowed to react[5] at 270 °C for 5 h in vacuo with a gentle stream of nitrogen introduced through a capillary. A pale yellowish copolymer was obtained in quantitative yield: mp 246 °C; η_{sp}/C = 1.81 (5.0 g/L in *m*-cresol at 30 °C); ^1H NMR (HCO_2H) δ 0.8 (m, $C(CH_2)C$), 1.9 (m, CH_2CO_2), 2.7 (m, NCH_2), 3.18 (s, OCH_2), 3.53 (s, OCH_2CO_2). In the polymer was detected no fraction soluble in either H_2O, methanol, or $CHCl_3$ (good solvents for poly(oxyethylene)). These data indicate that the product is a block copoly(amide–ether) consisting of the hard polyamide block and the soft poly(oxyethylene) block. A filament of this copolyamide was prepared by a melt-spinning technique and was drawn to four times its length at 50 °C. The filament obtained (diameter ≃80 × 10^{-6} m) showed an elastic flexibility. The following mechanical properties were found: maximum strength = 10 kg/mm^2, elongation at

0024-9297/83/2216-1023$01.50/0 © 1983 American Chemical Society