compared to random copolymers of the same composition.

Conclusion

As suggested by Brochard and de Gennes,[2] the use of permeability coefficient derived from sedimentation data by means of the Mijnlieff and Jaspers relation provides a very useful parameter for probing the hydrodynamic screening effect in semidilute solutions of flexible polymer chains. A comparison of permeability data for polystyrene in various solvents, based on the existing sedimentation data in the literature, shows that the values of this parameter are solvent-independent in both the limits of Θ and good solvent conditions. In Θ solvents its values are about 3 times greater than in good solvents, indicating an important hydrodynamic screening effect associated with the excluded volume effect present in the good solvent systems. The present data for 1,2-dibromoethane, a solvent with moderate affinity for PS, are close to the good solvent data, indicating that the crossover between the Θ and good solvent regime should occur in the vicinity of the Θ conditions. Therefore, it is not surprising that the extra excluded volume effect arising from heterocontact repulsive interactions in either homogenous block polymer solutions or random copolymer solutions scarcely affects their permeability behavior in solvent conditions remote from Θ conditions. Such behavior has been observed in the present study. The permeability data for styrene–isoprene diblock polymers in 1,2-dibromoethane are superimposable on the data obtained for homo-PS and homo-PI, the latter being fortuitously identical, while those for a random copolymer having about the same composition as the block polymers appear to be slightly displaced toward lower values. The smaller permeability for the random copolymer is consistent with the larger number of heterocontacts inherent in its random structure.

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Registry No. (Styrene)·(isoprene) (copolymer), 25038-32-8.

References and Notes

(1) Mijnlieff, P. F.; Jaspers, W. J. M. *Trans. Faraday Soc.* **1971**, *67*, 1837.

(2) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.

(3) Roots, J.; Nyström, B. *Polymer* **1979**, *20*, 148.

(4) Pouyet, G.; Dayantis, J. *Macromolecules* **1979**, *12*, 293.

(5) Destor, C.; Rondelez, F. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 527.

(6) Pouyet, G.; François, J.; Dayantis, J.; Weill, G. *Macromolecules* **1980**, *13*, 176.

(7) Roots, J.; Nyström, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 479.

(8) Vidakovic, P.; Allain, C.; Rondelez, F. *Macromolecules* **1982**, *15*, 1571.

(9) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.

(10) Corbin, N.; Prud'homme, J. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1937.

(11) Gallot, B. In "Liquid Crystalline Order in Polymers"; Blumstein, A., Ed.; Academic Press: New York, 1978; p 191.

(12) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093.

(13) Ho-Duc, N.; Prud'homme, J. *Int. J. Polym. Mater.* **1976**, *4*, 303.

(14) Billick, I. H. *J. Phys. Chem.* **1962**, *66*, 1941.

(15) Sung Gun Chu; Munk, P. *Macromolecules* **1978**, *11*, 101.

(16) Weill, G.; des Cloizeaux, J. *J. Phys. (les Ulis, Fr.)* **1979**, *40*, 99.

(17) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950; Vol. 1; 1965; Vol. 2.

(18) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979; p 263.

(19) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

Kinetics of the Degradation of Electrical Conductivity in Polypyrrole

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ABSTRACT: A kinetic study of the degradation of the electrical conductivity of polypyrrole is reported. Polypyrrole was synthesized with a variety of anions including the *p*-toluenesulfonate, perchlorate, and tetrafluoroborate anions. Two different kinetic processes were found depending on the choice of anion. One process followed first-order reaction kinetics and the other was multiorder. The degradation of the conductivity of polypyrrole/toluenesulfonate was found to obey first-order reaction kinetics, while the other dopants investigated followed multiorder kinetics.

Introduction

The development of conducting polymers can be traced to the mid-1970's when researchers at the University of Pennsylvania reported that films of polyacetylene could be rendered conducting by reaction (doping) with a suitable electron-withdrawing group or electron-donating group.[1] Since that time, several other conducting polymers have been discovered.[2] One class of these conducting polymers is the polyheterocycles such as polypyrrole and its chalcogen analogues. Polypyrrole is normally synthesized electrochemically,[3] and as a result of the simultaneous oxidation and polymerization of the pyrrole monomer, the conducting form of the polymer is actually an oxidized backbone (see Figure 1) with a delocalized positive charge on the π electron system. Electrical conduction is thought to occur by conduction of these "holes".[4] In order to maintain charge neutrality an anion from the electrolyte is incorporated into the polymer. Typical anions that are incorporated are perchlorate (ClO_4^-), tetrafluoroborate (BF_4^-), and *p*-toluenesulfonate (PTS).

Polyacetylene is the most investigated of the conducting polymers, and it is considered the prototypical conducting polymer. It has been the basis for many possible applications, ranging from Schottky-barrier-type devices to rechargeable batteries.[5] Although polyacetylene (undoped, p-doped, and n-doped) reacts with oxygen and water leading to a decrease in conductivity,[6] it still possesses potential utility if used in an inert atmosphere. This is because n-type polyacetylene (i.e., alkali metal doped) is thermally stable.[7] Many researchers have investigated the

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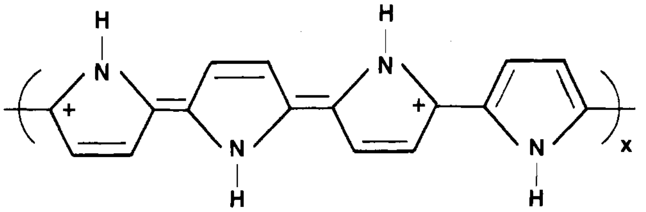

Figure 1. Structure of oxidized and electronically conducting polypyrrole.

dopant dependence on the thermal stability of p-doped polyacetylene.[8-14] In particular, Elsenbaumer et al.[14] observed mass loss in p-doped polyacetylene and correlated the mass loss with the conductivity decrease that occurs when polyacetylene is heated in an inert atmosphere. The kinetics of the mass loss followed first-order Arrhenius behavior and were independent of the dopants investigated. In a kinetic study of the degradation of the conductivity of p-doped polyacetylene in an inert atmosphere, Druy et al.[13] observed two different processes. One was dopant dependent and the other dopant independent. The dopant-independent process was also found to obey first-order reaction kinetics. In both the mass-loss study and the conductivity-loss study, the researchers postulated a mechanism of degradation that involved the formation of interchain cross-links. The formation of sp^3 centers as a result of the cross-linking reaction would lead to defects that would prohibit electrical conduction. Thus, it was determined that acceptor-doped polyacetylene was intrinsically unstable with respect to conductivity loss even if kept in an inert environment. It was predicted on the basis of the kinetics of the degradation process that acceptor–doped polyacetylene would lose one order of magnitude in conductivity for every 18 months storage at room temperature.[13]

Polypyrrole (in its oxidized conducting form) has been found by many investigators to possess reasonable stability in air toward the degradation of conductivity and been the subject of thermal experiments in which it was found to be stable to mass loss up to 180 °C.[15] Additionally Salmon et al. observed that polypyrrole doped with perchlorate, tetrafluoroborate, and hexafluorophosphate lost conductivity and decomposed at ca. >150 °C in air and toluenesulfonate-containing films did not decompose until 280 °C. Although a dependence of stability on anion was reported, it was not evident from this study whether the dependence was due to a decreased reactivity of the dopant/polymer system with oxygen and moisture or due to decreased reactivity between the dopant and polymer themselves. In other words, was an intrinsic or extrinsic stability measured?

Detailed investigations have been carried out at GTE Laboratories to identify the role of the dopant anion in the degradation of electrical conductivity in polypyrrole. In order to determine if the conductivity degraded as a result of dopant degradation or dopant reaction with the polymer backbone, polypyrrole was heated in an inert atmosphere and its conductivity was measured before and after heating. The kinetics of the degradation process were also followed in air in order to identify the nature of the degradation process. Our findings further establish the inherent stability of polypyrrole and the importance of the dopant in determining the environmental and intrinsic stability of conducting polymers.

Thus, the focus of this paper is to report on this investigation of the inherent stability of the polypyrrole system and the role of the dopant in the degradation process and to address questions regarding the kinetics of the degradation process of conductivity in polypyrrole.

Experimental Section

Pyrrole monomer (Aldrich) was distilled under nitrogen before use and simultaneously oxidized and polymerized in a three-compartment cell under galvanostatic control. The current density was 0.6–0.8 mA/cm^2. The solvents and electrolyte combinations were as follows: 1 M lithium perchlorate ($LiClO_4$)/THF, 0.3 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4)/THF, and 0.25 M tetraethylammonium *p*-toluenesulfonate (Et_4NPTS)/acetonitrile or propylene carbonate. Lithium perchlorate (G. F. Smith Co.) was dried at 105 °C under dynamic vacuum for 36 h and then melted and cooled under dynamic vacuum prior to use. Tetrabutylammonium tetrafluoroborate (Southwestern Analytical) was dried overnight at 105 °C under dynamic vacuum before use. Tetraethylammonium *p*-toluenesulfonate (Aldrich) was used as received. Tetrahydrofuran (THF) and acetonitrile were dried as previously described.[16,17] Propylene carbonate (Burdick and Jackson) was used as received. All electrochemical polymerizations were performed in an inert-atmosphere glovebox except as discussed below. Conductivity measurements were performed with a four-probe arrangement, and a pressure contact was made between the platinum wires and the film.

The doped samples were heated in an inert atmosphere and in laboratory air. The following dopants were evaluated: ClO_4^- (perchlorate), BF_4^- (tetrafluoroborate), and $CH_3C_6H_4SO_3^-$ (toluenesulfonate). The samples were mounted via a pressure contact to a glass four-probe cell that was fitted with a ground joint and a stopcock such that the cell could be evacuated and backfilled with the desired atmosphere. Each doped sample was heated in an oil bath while exposed to laboratory air. The four-probe resistance was monitored in situ, and the experiment was carried out for 900 min. The samples were heated at 100, 125, and 150 °C, and a fresh sample was used for each heating run. The four-probe resistance of the samples was also monitored at room temperature (22 °C) in laboratory air.

Results

Many investigators have observed the effect of dopant on the physical properties of polypyrrole. In particular, Salmon et al.[18] observed that kinetics of the electrochemical switching response were influenced by the choice of anion. It was postulated that the size of the anion and its ability to diffuse in and out of the film affected the shape of the cyclic voltammogram and thus the kinetics of the oxidation and reduction of polypyrrole.

Additionally, as was previously mentioned, the thermal stability of polypyrrole was influenced by the choice of anion. More recently, Diaz observed a dependence of the mechanical properties on the choice of anion. Polypyrrole synthesized in the presence of perchlorate and tetrafluoroborate tended to be less ductile and weaker than polypyrrole synthesized in the presence of toluenesulfonate.[15] The authors of the previous study suggested that chemical differences between the anions could be responsible for the various properties, which were observed to depend on the choice of the anion. It was our intention to examine the kinetics of the degradation process in air of polypyrrole doped with a variety of anions in the hope of identifying different degradation pathways for the degradation of electrical conductivity in polypyrrole as a function of anion.

Figure 2 shows the data for the combination of polypyrrole and toluenesulfonate. Similar data was obtained from the other samples. This figure contains the data from the runs at 100, 125, and 150 °C. The data is plotted as a function of log R_t/R_0 vs. time (min). R_t represents the resistance of the sample at the temperature of the experiment at a given time. R_0 represents the resistance of the sample at the temperature of the experiment at time zero. The data is fit to a linear function, i.e.

$$\log R_t/R_0 = kt \quad (1)$$

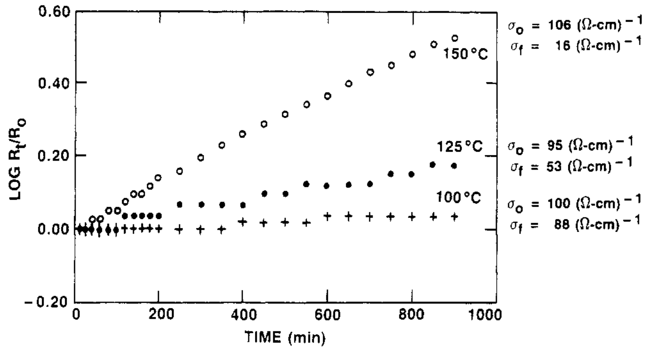

Figure 2. log R_t/R_0 vs. time (min) exposed to air at elevated temperature for polypyrrole/toluenesulfonate. R_t is the resistance of the sample at the temperature of the experiment at a given time. R_0 is the resistance of the sample at the temperature of the experiment at time zero.

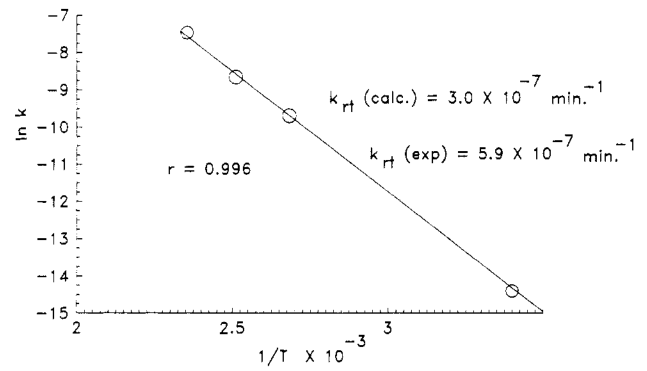

Figure 3. ln k vs. $1/T$ (K) for polypyrrole/toluenesulfonate. Rate constants, k, are from Table I. r is the correlation coefficient for line drawn through points.

Table I
Rate Constants for Polypyrrole/Toluenesulfonate, Polypyrrole/Tetrafluoroborate, and Polypyrrole/Perchlorate from Fitting Data to Eq 1 (See Text)

sample	temp, °C	rate constant k, min^{-1}
polypyrrole/toluenesulfonate	22	5.9×10^{-7}
	100	6.8×10^{-5}
	125	1.8×10^{-4}
	150	5.9×10^{-4}
polypyrrole/tetrafluoroborate	22	2.1×10^{-6}
	100	1.2×10^{-4}
	125	4.2×10^{-4}
	150	5.5×10^{-4}
polypyrrole/perchlorate	22	5.7×10^{-7}
	100	9.2×10^{-5}
	125	2.4×10^{-4}
	150	3.3×10^{-4}

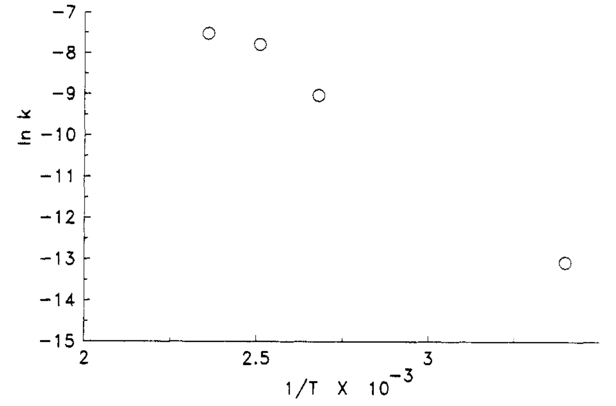

Figure 4. ln k vs. $1/T$ (K) for polypyrrole/tetrafluoroborate. Rate constants, k, are from Table I.

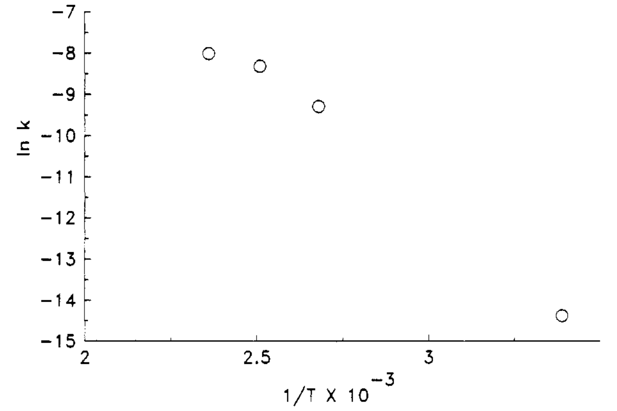

Figure 5. ln k vs. $1/T$ (K) for polypyrrole/perchlorate. Rate constants, k, are from Table I.

Table II
Conductivity of Polypyrrole/Toluenesulfonate, Polypyrrole/Perchlorate, and Polypyrrole/Tetrafluoroborate before and after Heating in Nitrogen for 900 min

	conductivity, (ohm·cm)$^{-1}$		
sample	temp, °C	before	after
polypyrrole/PTS	100	31	40
	100	71	74
	125	64	69
	125	122	123
	150	35	40 (4 days)
	150	25	28
	150	62	69 (4 days)
	200	65	42
polypyrrole/perchlorate	100	98	70
	125	70	35
	125	49	19 (4 days)
polypyrrole/tetrafluoroborate	100	85	117
	125	125	165
	125	84	96
	150	96	90
	150	115	90

where k is the slope of the line and the rate constant for the degradation process. In this case the y intercept is assumed to be zero, i.e., log $R_t/R_0 = 0$ when $t = 0$. The natural logarithm of each rate constant is then plotted as a function of inverse temperature (in Kelvin). By doing this we are assuming first-order reaction kinetics. The plot is fit to eq 2 where R is 0.00197 kcal/(mol·K), E is the

$$k = Ae^{-E/RT} \quad \text{or} \quad \ln k = -E/RT \qquad (2)$$

activation energy for the degradation process, and T is the temperature in Kelvin. Thus the slope of this line is the activation energy for degradation of the conductivity in air. The rate constants for polypyrrole doped with the toluenesulfonate, tetrafluoroborate, and perchlorate anions are listed in Table I for each of the four temperatures. The plot of ln k vs. inverse temperature is shown in Figures 3–5 for polypyrrole/toluenesulfonate, polypyrrole/tetrafluoroborate, and polypyrrole/perchlorate, respectively. The data shown in Figure 3 are for a polypyrrole/toluenesulfonate film that was made in laboratory air. Otherwise all other samples were made in an inert-atmosphere glovebox with rigorously dried solvents and electrolytes. In a separate experiment polypyrrole/toluenesulfonate was prepared under identical conditions as polypyrrole/perchlorate and polypyrrole/tetrafluoroborate. Its nonlinear kinetic behavior was found to be similar to that of the perchlorate- and tetrafluoroborate-doped samples.

In a separate experiment, polypyrrole/toluenesulfonate (made in laboratory air), polypyrrole/tetrafluoroborate, and polypyrrole/perchlorate were heated in sealed tubes in a dry nitrogen/vacuum atmosphere. The conductivities of the samples were measured before and after heating, and the samples were heated at 100, 125, and 150 °C. Table II shows the results of this experiment.

Discussion

From examination of the data in Figures 3–5, we conclude the following points. The first is that the behavior of polypyrrole/toluenesulfonate is first order and that polypyrrole/tetrafluoroborate and polypyrrole/perchlorate are not first order in their degradation of the conductivity. In other words, the degradation of the conductivity when polypyrrole/toluenesulfonate is exposed to air appears to be a process that follows first-order reaction kinetics; i.e., reaction of the polymer backbone with air. On the other hand, the degradation of conductivity of polypyrrole/tetrafluoroborate and polypyrrole/perchlorate does not follow first-order reaction kinetics. Consideration of the results in Table II suggests that in the case of tetrafluoroborate- and perchlorate-doped polypyrrole, there is another reaction that results in the degradation of conductivity when these materials are heated in an inert atmosphere. It should be noted that under identical conditions, the conductivity of toluenesulfonate-doped polypyrrole did not degrade (see Table II). The causes of the decrease of conductivity in perchlorate- and tetrafluoroborate-doped polypyrrole when it is heated in an inert atmosphere may be due to degradation of the dopant and subsequent reaction of the products of the degradation with the polymer backbone or a reaction between the dopant and polymer backbone that results in a loss of conductivity.

Since the behavior of polypyrrole/toluenesulfonate follows first-order reaction kinetics, we can calculate the activation energy for the degradation process from eq 2 and the slope of the line in Figure 3. The calculated activation energy is 15 kcal/mol. Knowing the activation energy and a rate constant for the degradation at a specific temperature, we can calculate a rate constant for the degradation of the conductivity at room temperature. The calculated rate constant is 3.0×10^{-7} min^{-1}. Thus, there is very good correlation between the calculated and experimental (see Table I) rate constants.

The experimental room temperature rate constant represents a one order of magnitude loss in conductivity for every 3 years exposure to laboratory air for polypyrrole/toluenesulfonate that was synthesized in laboratory air.

Experiments aimed at understanding the degradation process of the polypyrrole/toluenesulfonate process in more detail are currently under way and will be reported in a future paper. We are also investigating the different possible degradation pathways present in polypyrrole/toluenesulfonate made in laboratory air and polypyrrole/toluenesulfonate made in the absence of laboratory air. Additionally it should be mentioned that the effect of the counterion on the intrinsic and extrinsic stability could be more indirect than that mentioned above. For example, the effect of the anion might be to alter the crystallinity of the polymer/dopant system, the content of chemical defects, or extent of backbone oxidation. All of these may effect the reactivity of the dopant/polymer system to the environment and its thermal stability.

Conclusions

We have investigated the effect of dopant on the kinetics of the degradation of electrical conductivity of polypyrrole when it is heated in laboratory air and exposed to laboratory air at ambient conditions. In particular we have found two different kinetic processes for the degradation of conductivity. One follows first-order reaction kinetics, and the other appears to be a more complex process. The degradation mechanism that follows first-order kinetics may be a reaction of the delocalized carbonium ion along the polymer backbone with oxygen or water. Polypyrrole/toluenesulfonate (prepared in laboratory air) is an example of this phenomenon. The other degradation mechanism is most likely a combination of two or more processes. One is the reaction of the polymer backbone with the dopant anion, and the other is the reaction of the polymer backbone with oxygen or water. Additionally it is possible that the dopant species itself might undergo thermal degradation and the products of this degradation could react with the polymer backbone. Polypyrrole/perchlorate is an example of this degradation mechanism.

We have also demonstrated for the first time the capability to predict adequately the environmental stability of a conducting polymer on the basis of a kinetic treatment of accelerated life tests. The data we obtained and analyzed for polypyrrole/toluenesulfonate suggests a one order of magnitude loss of conductivity for every 3 years exposure to air at ambient conditions. Since the degradation mechanism appears to follow first-order reaction kinetics and may involve the reaction of the delocalized carbonium ion backbone with oxygen or water, it should be possible to improve the environmental stability with encapsulation.

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Registry No. PTS, 16722-51-3; ClO_4^-, 14797-73-0; BF_4^-, 14874-70-5; polypyrrole, 30604-81-0.

References and Notes

(1) Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978**, *100*, 1013.

(2) See, for example: Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals, *Mol. Cryst. Liq. Cryst.* **1985**, 117, 118.

(3) Kanazawa, K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Raboldt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.

(4) Kanazawa, K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1980**, *1*, 329.

(5) Ozaki, M.; Peebles, D.; Weinberger, B. R.; Heeger, A. J.; MacDiarmid, A. G. *J. Appl. Phys.* **1980**, *51*, 4252. Waldrop, J. R.; Cohen, M. J.; Heeger, A. J.; MacDiarmid, A. G. *Appl. Phys. Lett.* **1981**, *38*, 53. Grant, P. M.; Tani, T.; Gill, W. D.; Krounbi, M.; Clarke, T. C. *J. Appl. Phys.* **1981**, *52*, 869. MacInnes, D., Jr.; Druy, M. A.; Nigrey, P. J.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 317.

(6) Park, Y. W.; Heeger, A. J.; Druy, M. A.; MacDiarmid, A. G. *J. Chem. Phys.* **1980**, *73*, 946.

(7) Elsenbaumer, R. L.; Miller, G. G.; Baughman, R. H. U.S. Patent 4 502 981.

(8) Weber, D. C.; Holtzclaw, J. R.; Pron, A. B.; Brant, P.; Wyatt, J. R.; Decorpo, J. J.; Saalfeld, F. E. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *40*, 101.

(9) Allen, W. N.; Decorpo, J. J.; Saalfeld, F. E.; Wyatt, J. R.; Weber, D. C. *Synth. Met.* **1979**, *1*, 371.

(10) Rolland, M.; Lefrant, S.; Aldissi, M.; Bernier, P.; Rzepka, E.; Shue, F. *J. Electron Mater.* **1981**, *10*, 619.

(11) Osterholm, J. E.; Yasuda, H. K.; Levenson, L. L. *J. Appl. Polym. Sci.* **1983**, *28*, 1265.

(12) Huq, R.; Farrington, G. C. *J. Electrochem. Soc.* **1984**, *131*, 819

(13) Druy, M. A.; Rubner, M. F.; Walsh, S. P. *Synth. Met.* **1986**, *13*, 207. Druy, M. A.; Rubner, M. F.; Walsh, S. P. *Electrochem.*

Soc. Extended Abst. **1984**, *2*, 897.
(14) Elsenbaumer, R. L.; Miller, G. G.; Khanna, Y. P.; McCarthy, E.; Baughman, R. H. *Electrochem. Soc. Extended Abst.* **1985**, *1*, 118.
(15) Diaz, A. F.; Hall, B. *IBM J. Res. Dev.* **1983** *27*, 342.
(16) Druy, M. A. *J. Electrochem. Soc.*, in press.
(17) Druy, M. A.; Seymour, R. J.; Tripathy, S. K. *ACS Symp. Ser.* **1984**, *No. 242*, 473.
(18) Salmon, M.; Diaz, A. F.; Logan, A. J.; Krounbi, M.; Bargon, J. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 265.

Experimental Study of the Density Recovery of Pressure-Densified Polystyrene Glasses

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ABSTRACT: Densities were measured vs. time at various annealing temperatures (65, 80, and 95 °C) for polystyrene glasses vitrified at various pressures and cooling rates. Results show that the rate of density change at early times is much more rapid for samples formed at high pressures and cooling rates. A minimum density or "undershoot" was observed, the magnitude of which increased with vitrification pressure and cooling rate. For each annealing temperature, all samples attained the same constant density at long times, independent of vitrification conditions. Samples vitrified at atmospheric pressure, despite the initially greater free volume and smallest displacement from equilibrium, recovered slowest and took longer to reach these constant densities. Densities were measured by density gradient columns at 23 °C.

Introduction

Measurements of density or specific volume with time are a common means to characterize physical aging or recovery of polymeric glasses below T_g.[1-5] In most experiments, the material is subjected to various thermal histories or annealing treatments prior to measurements. Indeed, the temperature-jump experiments of Kovacs[3] and subsequent theories to describe volume changes with time provide valuable insight into the volume-recovery mechanism.[6-13] Density, however, is affected not only by thermal history but to a greater extent by solidification pressure.[14-20] The effect of pressure on recovery rate is important from a theoretical viewpoint by presenting data that will allow a greater refinement of current theories and from a practical viewpoint because processing methods like injection molding involve materials solidifying under elevated pressure. It is well established that applied pressure changes the glass transition temperature, and subsequent cooling of the materials through T_g while under applied pressure significantly affects volume recovery. In this report we investigate the effects of solidification pressure and cooling rate on the aging of glassy polystyrene at atmospheric pressure.

In the pressure-step experiment the glass is cooled from the liquid state through the glass transition temperature under hydrostatic pressure. When the glass attains ambient temperature, the pressure is suddenly released. Following the depressurization step, the glasses are annealed at temperatures near the glass transition temperature. The changes in density occurring during the annealing process are measured by density gradient column at 23 °C.

Density gradient columns were used because they allowed us to use very small samples, thus minimizing density inhomogeneities within the samples and time to reach thermal equilibrium before meaningful measurements could be made. This is particularly important because recovery can occur rapidly within the first few minutes for some sample preparations.

Experimental Section

Materials. The polystyrene used was a Dow special additive-free grade in the form of transparent pellets. The pellets measured about 3 mm in length and 1.5 mm in diameter. Each pellet weighed about 30 mg with MW = 3.1×10^5 and $M_w/M_n = 2.78$ as determined by GPC analysis.

Equipment. Pressure-densified glasses were prepared with the apparatus diagrammatically illustrated in Figure 1. The pressure source was a Teledyne-Sprague Engineering high-pressure, air-driven hydraulic pump (No. s-216-cs-700-ss), which was capable of 500 MPa from a 0.7-MPa air line. Samples in pellet form were individually wrapped in Teflon tape, stacked into the high-pressure cylinder, and covered with purified mercury. A resistance heating jacket was placed around the cylinder and connected to a controller–power supply. A thermocouple used for temperature control was placed into a small hole drilled directly into the pressure vessel. Temperature control and cooling rate programming were accomplished by an Omega Engineering Model 49 proportioning control unit that was connected to an R.I. Controls Model FGE 5110 Data-Trak cooling rate controller.

Three annealing ovens were set up for long-term annealing (24 h to 1 year) at the following temperatures, 95 °C (±0.14 °C) (Ransco Industry temperature test chamber no. SD 30-1), 80 °C (±0.5 °C) (Central Stabil-Therm constant-temperature cabinet), and 65 °C (±0.5 °C) (Central Scientific Co. constant-temperature appliance, no. 98308).

A specially modified oven (Delta Design Inc. temperature test chamber Model No. 6545-S) was used for short-term annealing (70 s to 24 h). This oven allowed quick removal of the samples required for short annealing time. Samples were annealed at the same temperatures stated above, i.e., 95, 80, and 65 °C.

Approximately 30 pellets were compressed per pressurization experiment. These samples were compressed at ambient temperature and heated 10–20 °C above the glass transition temperature calculated for each pressure. The sample remained compressed at least 45 min to allow it to equilibrate. The applied pressures used were atmospheric, 69 MPa (10 000 psi), 138 MPA (20 000psi), 207 MPA (30 000psi), and 276 MPa (40 000 psi). The two cooling rates used were 3.3×10^{-3} °C/s (slow-cooled) and 5 °C/s, obtained by fast-cooling into ice water. In either case the samples were cooled to about 23 °C, and the pressure was released. The densified glasses were unwrapped, placed into a Buchner funnel, and washed with cold distilled water. After the samples were cleaned, they were placed into a Sorvall superspeed angled centrifuge (Type SS-1-A) and spun in a low-density cold sodium bromide solution. This procedure helped eliminate air from any microcracks in the surface of the samples and resulted in precise

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