Viscosity Characterization of an Alternating Copolymer of Ethylene and Tetrafluoroethylene

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ABSTRACT: Viscosity measurements on dilute solutions of an alternating copolymer of ethylene and tetrafluoroethylene (PETFE) in diisobutyl adipate have been performed at 240 °C. $[\eta] = 2.3 \times 10^{-3} M_w^{0.71}$ (mL/g) with M_w expressed in grams per mole, in fairly good agreement with the result based on the diffusion exponent $\alpha_D = 0.58$ in which $\alpha_\eta = 3\alpha_D - 1 \approx 0.74$. When the solvent viscosity is combined with previous laser light scattering characterizations of the same polymer solutions, the hydrodynamic radius (R_h) and the ratio of R_h/R_g can be computed where R_g is the radius of gyration. As $R_h/R_g = 1.29$, 0.663, and ~0.54 for a hard sphere, a Gaussian coil, and an expanded coil, respectively, a value of ~0.58 suggests that the PETFE copolymer in diisobutyl adipate at 240 °C forms slightly expanded coils as in a fairly good solvent.

1. Introduction

Laser light scattering (LLS) has been used successfully to characterize an alternating copolymer of ethylene and tetrafluoroethylene (denoted as PETFE) in diisobutyl adipate at 240 °C.[1-3] Three PETFE copolymers, known as TEFZEL (a registered trademark of Du Pont) 210, 200, and 280, were used in the LLS characterization in which the weight-average molecular weight M_w, the z-average translational diffusion coefficient at infinite dilution D^0, and the root-mean-square radius of gyration R_g of the copolymers yielded

$$R_g\,(\text{nm}) = 2.04 \times 10^{-2} M_w^{0.58} \quad (1)$$

$$D^0\,(\text{cm}^2/\text{s}) = 8.89 \times 10^{-4} M_w^{-0.58} \quad (2)$$

with M_w expressed in grams per mole. In this paper, we present details of our viscosity studies on dilute PETFE solutions of the same copolymer samples in diisobutyl adipate at 240 °C. When viscosity results are combined with the LLS characterization, both the hydrodynamic radius R_h and the ratio of R_h/R_g can be computed. Thus, we are able to confirm the diffusion exponent $\alpha_D \approx 0.58$ and the nature of the TEFZEL coils in diisobutyl adipate at 240 °C. Furthermore, the establishment of the intrinsic viscosity $[\eta]$-molecular weight relationship shall provide an easier procedure for molecular weight characterizations of TEFZEL based on viscosity measurements of dilute polymer solutions.

2. Experimental Methods

2.1. Preparation of Solvent. Oligomers of chlorotrifluoroethylene and diisobutyl adipate are the few known solvents that have been used successfully to dissolve TEFZEL. As the oligomers are mixed solvents with viscosities depending upon the oligomer molecular weight distribution and composition, we have chosen diisobutyl adipate as the reference solvent. Diisobutyl adipate from Hatco Industries was purified by passing it through a column of activated silica gel to remove acidic and basic impurities that caused discoloration at high temperatures. The resulting material was 99.5% pure by vapor phase chromatography. The physical properties of diisobutyl adipate at room temperatures could be obtained from the handbook:[9] bp 282 °C at 760 mmHg and density = 0.953 g/mL at 20 °C.

Table I
Molecular Parameters of TEFZEL Copolymers[1-3]

sample	M_w, g/mol	M_w/M_n[a]	R_g, nm	D^0, cm²/s	R_h,[b] nm
TEFZEL 210	5.4×10^5	1.3	45.4	4.21×10^{-7}	26.6
TEFZEL 200	9.0×10^5	1.3	61.9	3.13×10^{-7}	35.8
TEFZEL 280	1.16×10^6	1.4	72.1	2.70×10^{-7}	41.5

[a] The polydispersity index M_w/M_n was based the time correlation function profile analysis using Provencher's CONTIN regularization method.[4] [b] This work with $\eta^0 = 0.335$ cP and the use of the Stokes-Einstein relation.

2.2. Copolymer Characteristics. Three commercial grades of TEFZEL 210, 200, and 280 produced by E. I. du Pont de Nemours & Co., Inc., were used in the present study. They were characterized by laser light scattering[1-3] with the molecular parameters listed in Table I.

2.3. Preparation of Solutions. The polymer solutions at different concentrations were prepared by dissolving a known weight of TEFZEL directly in a known volume of filtered (by Millipore FG filter with a nominal pore diameter of 0.5 μm) diisobutyl adipate in the reservoir of the viscometer (1) at 250 °C. It took about 2 h for a complete dissolution of the TEFZEL copolymer and for the solution to reach a homogenous state. The homogenous mixing was accomplished by introducing a glass-coated magnetic stirring bar that could be activated by an external magnet. The polymer solution concentration could be determined by varying known amounts of solvent or polymer in the viscometer reservoir. The concentrations of the TEFZEL/diisobutyl adipate solutions studied are listed in Table II.

2.4. High-Temperature Capillary Viscometer. A new high-temperature capillary viscometer for measuring the viscosity of dilute polymer solutions has been designed, constructed, and tested with the details being described elsewhere.[5] The high-temperature viscometer had a large thermal bath consisting of a 40 cm × 30 cm (diameter × height) glass cylinder jar that was insulated with half-inch thick silicone rubber. The thermal bath had another sealed aluminum cylinder jacket outside the silicone rubber insulation in the event of glass jar breakage. For high-temperature operations up to 250 °C, the thermal bath

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Table II
Reduced Viscosity of TEFZEL/Diisobutyl Adipate Solutions as a Function of Concentration

sample	TEFZEL 210 C, g/mL	η_{sp}/C, mL/g	TEFZEL 200 C, g/mL	η_{sp}/C, mL/g	TEFZEL 280 C, g/mL	η_{sp}/C, mL/g
1	9.50×10^{-4}	27.9	6.50×10^{-4}	39.2	1.30×10^{-3}	48.9
2	2.15×10^{-3}	28.3	9.50×10^{-4}	39.4	1.35×10^{-3}	49.0
3	3.00×10^{-3}	28.4	2.55×10^{-3}	40.1	2.40×10^{-3}	49.7
4					2.65×10^{-3}	49.8

was filled with a Krytox (a registered Du Pont trademark) vacuum pump fluid (16256, perfluoroalkyl polyethers) that remained transparent and had a fairly low vapor pressure until 280 °C. Thus, the limit of our high-temperature capillary viscometer was determined mainly by the thermostat oil used. At 250 °C, the Krytox oil was slightly volatile so that the thermal bath should be operated in a well-vented hood. Hydrogen fluoride might be released at temperatures above 280 °C precluding the use of normal glass immersion heaters because of the higher temperature at the glass/oil interface. With three stirrers and heaters strategically located, the large thermal bath could be controlled to ±0.01 °C at 250 °C. The viscometer system had a dual precision timer/counter[6] capable of flow time measurements to better than ±0.001 s. With a temperature control of ±0.01 °C, the flow time measurement for an individual viscometer was precise to ±0.01 s. However, our viscometer system had a twin viscometer arrangement; i.e., the two viscometers (one for the solution and the other for the solvent) were closely coupled together by a thick aluminum plate that was also immersed in the thermal bath. Thus, flow time variations due to local temperature fluctuations were minimized. With a temperature fluctuation of ±0.005 °C, the flow time measurements of the twin viscometer could agree to ±0.000 04 (standard deviation). With temperature fluctuations of ±0.04 °C, the flow time agreed to ±0.0002. The viscometer could be positioned at three different angles of inclination yielding three different shear rates.

The viscometer was calibrated by *o*-xylene and verified by *n*-decane. All the measurements on polymer solutions were completed in 12 h. The solvent became yellow if it stayed at 240 °C for longer periods of time. Two independent sets of viscosity measurements were carried out on diisobutyl adipate from 60 °C to 240 °C. The two sets of data agreed very well.[5] Reduced viscosity data for the three TEFZEL polymers are listed in Table II.

3. Results and Discussion

3.1. Viscosity of Diisobutyl Adipate. With the solvent viscosity, the hydrodynamic radius can be computed from the diffusion coefficient at infinite dilution D^0 by using the Stokes–Einstein relation.

We have not only determined the viscosity of diisobutyl adipate at 240 °C but also established the viscosity–temperature dependence

$$\ln \eta \text{ (cP)} = -4.70 + 1.85 \times 10^3/T \text{ (K)} \quad (3)$$

with a fitting coefficient of 0.9997. The viscosity of diisobutyl adipate at 240 °C has a value of 0.335 cP.

3.2. Intrinsic Viscosity [η] of TEFZEL/Diisobutyl Adipate Solution. A widely used empirical equation that relates the reduced viscosity η_{sp}/C to the concentration C is the Huggins equation

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2C \quad (4)$$

where η_{sp} [$= (\eta - \eta_0)/\eta_0$] is the specific viscosity with η and η_0 being the viscosities of the solution and the solvent, respectively. Furthermore, at sufficiently low concentrations, the Kraemer equation also holds

$$\ln \eta_r/C = [\eta] - K_K[\eta]^2C \quad (5)$$

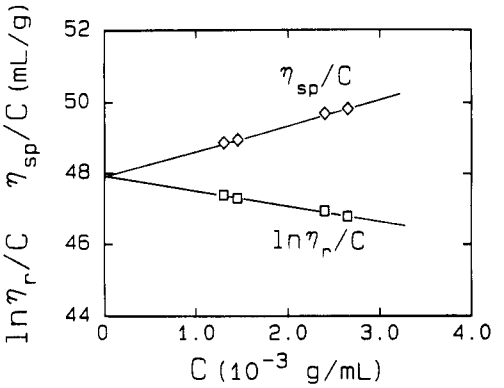

Figure 1. Typical plot of η_{sp}/C (hollow diamonds) and ($\ln \eta_r/C$) (hollow squares) versus concentration C for TEFZEL (280, $M_w = 1.16 \times 10^6$ g/mol) in diisobutyl adipate at 240 °C. The solid lines are presented in eq 7 and 8.

Table III
Intrinsic Viscosities and Huggins and Kraemer Coefficients (K_H and K_K) for TEFZEL in Diisobutyl Adipate at 240 °C

sample	M_w, g/mol	[η], mL/g	K_H	K_K
TEFZEL 210	5.4×10^5	27.7	0.304	0.186
TEFZEL 200	9.0×10^5	38.9	0.318	0.178
TEFZEL 280	1.16×10^6	47.9	0.314	0.184

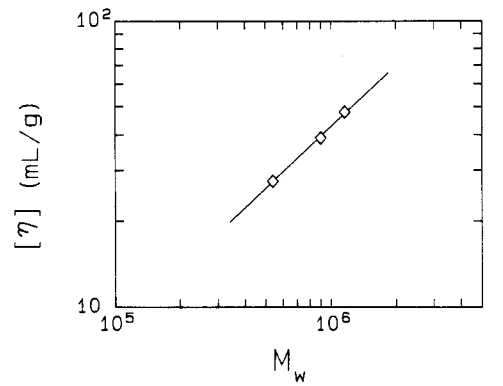

Figure 2. log–log plot of [η] versus M_w using data listed in Table III. The solid line is represented by eq 9.

with relative viscosity η_r being η/η_0. Thus

$$[\eta] = \lim_{C \to 0} \eta_{sp}/C = \lim_{C \to 0} (\ln \eta_r)/C \quad (6)$$

Figure 1 shows a typical double plot of TEFZEL (280, $M_w = 1.16 \times 10^6$) in diisobutyl adipate at 240 °C. From a linear least-squares fitting of the experimental data, we have

$$\eta_{sp}/C = 47.9 + 720C \text{ (mL/g)} \quad (7)$$

$$\ln \eta_r/C = 47.9 - 432C \text{ (mL/g)} \quad (8)$$

Thus, we obtained the intrinsic viscosity [η] = 47.9 mL/g for TEFZEL 280 in diisobutyl adipate, and $K_H = 0.314$ implying that diisobutyl adipate is a good solvent for TEFZEL at 240 °C. Intrinsic viscosities as well as the Huggins and Kraemer constants (K_H and K_K) are listed in Table III.

Figure 2 shows a log–log plot of [η] versus M_w for TEFZEL in diisobutyl adipate at 240 °C. We obtained

$$[\eta] = 2.3 \times 10^{-3} M^{0.71} \text{ (mL/g)} \quad (9)$$

Here, $\alpha_\eta = 0.71$. If we take $1 + \alpha_\eta = 3\alpha_D$,[7] we get $\alpha_D \approx 0.57$, in good agreement with $\alpha_D \approx 0.58$ from eq 2. Thus, diisobutyl adipate is a fairly good solvent for TEFZEL at 240 °C.

If we take η_0 = 0.335 cP for diisobutyl adipate at 240 °C, we can compute the hydrodynamic radius R_h for the TEFZEL copolymers with the results also listed in Table I. The ratio of $R_h/R_g \approx 0.58$. As R_h/R_g = 1.29, 0.663, and ~0.54[8] for a hard sphere, a Gaussian coil, and an expanded coil, respectively, a value of 0.58 for the R_h/R_g ratio again suggests that PETFE copolymer in diisobutyl adipate at 240 °C forms slightly expanded coils, indicating fairly good solubility.

In conclusion, our viscosity data are in good agreement with our previous light scattering characterizations of TEFZEL in diisobutyl adipate and the TEFZEL copolymer forms slightly expanded coils in diisobutyl adipate at 240 °C. We have now established a high-temperature viscosity reference that is experimentally simple to perform for the characterization of TEFZEL.

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Structural Coarsening of Demixed Polymer Solutions†

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ABSTRACT: The structural coarsening of demixed polystyrene/cyclohexane solutions was studied by using a quick freeze/freeze-dry technique on solutions allowed to coarsen for various lengths of time. Quenches of near-critical solutions were bicontinuous; however, the coarsening law was found to be consistent with a diffusive coarsening mechanism rather than the expected hydrodynamic flow mechanism. The structural size was found to grow with time with an exponent in the range 0.18–0.32. A quantitative model of the diffusive coarsening process was developed specifically for demixed polymer solutions, and predicted the structural sizes within a factor of 5 of the measured values. The model also predicted a very strong concentration dependence of coarsening, which was experimentally verified. An explanation as to why diffusive coarsening rather than coarsening by hydrodynamic flow occurs is offered.

Introduction

Thermally induced phase separation (TIPS) of polymer solutions is a commonly used technique to prepare microcellular foams or membranes with controlled morphologies. For example, low-density microcellular foams have been prepared with TIPS using many different polymers including atactic polystyrene,[1] isotactic polystyrene,[2] poly(4-methyl-1-pentene),[3] polyacrylonitrile,[4] and many water-soluble polymers such as (carboxymethyl)cellulose,[5] poly(acrylic acid),[6] and dextran.[7] An even larger variety of polymers have been used to prepare higher density foams and membranes.[8] TIPS is effective if the polymer solution exhibits an upper critical solution temperature. It differs from the more traditional approach to induce phase separation, which involves diffusing a nonsolvent into a polymer solution.[9] If the phase separation results in an interconnected polymer-rich phase, then a foam or membrane can be produced with two additional steps. The polymer-rich phase must be immobilized, either by gelation (crystallization) or by freezing of the solution. Finally the solvent must be removed by extraction and supercritical drying of a resultant gel or by sublimation under vacuum of a frozen solution. The type of phase separation and the rate of phase separation determine the ultimate morphology and properties of the membrane or foam. This has been demonstrated with well-characterized polystyrenes.[1,2]

Usually liquid phase separation creates a fine-scaled, "early-stage" structure in the polymer solution, which can be "frozen-in" if the polymer solution gels or if the quench is continued to a low enough temperature so that the solvent freezes. Estimates of the size expected for deep quenches into the spinodal region of polymer solutions have been made[1,10] and typically fall in the range 0.1–1.0 μm. This corresponds to some multiple of the polymers root mean square radius of gyration. The estimates are based upon the Cahn[11] theory for spinodal decomposition as modified by Van Aartsen[10] for polymer solutions. The dynamics of phase separation can also be calculated from Van Aartsen's theory. For polymer solutions the dynamics of early-stage structure development are expected to be very fast, perhaps even experimentally inaccessible for deep quenches. We have previously argued that the structures observed in freeze-dried polystyrene solutions quenched near their critical concentrations almost certainly correspond to coarsened

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