The Solubility of Tetrafluoroethylene/Hexafluoropropylene Copolymers

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The copolymers of TFE (tetrafluoroethylene) and HFP (hexafluoropropylene) form stable solutions in perfluorocarbons at much lower temperatures than TFE homopolymer (PTFE). Most of the work has emphasized the use of fused, 6-membered ring, aliphatic perfluorocarbons as solvents. Polymer concentrations as high as 10% were obtained; much higher concentrations are possible. Widely different solubility characteristics were found for several perfluorocarbon solvents suggesting the feasibility of fractionation via extraction to determine comonomer and end group distribution.

KEY WORDS Perfluoropolymer, solubility, poly(tetrafluoroethylene-cohexafluoropropylene), copolymer, perfluorocarbon

INTRODUCTION

This report deals with dissolution studies for the copolymers of tetrafluoroethylene (TFE) with hexafluoropropylene (HFP), about which little has been written. Like the homopolymers of TFE, the HFP copolymers are semicrystalline. This means that the first step in dissolution is melting the crystalline phase. Once melted, however, dissolution is not ensured since liquid-liquid phase separation can also occur [1]. The solution properties of these copolymers, like the homopolymer, should be dominated by entropy effects when dealing with non-polar solvents like perfluorocarbons. Thus, molar volume is one of the primary variables controlling melting point depression of the solution as well as liquid-liquid phase separation above the solution melting point. Decreasing molar volume increases the single-phase solubility region by both decreasing the melting point and increasing the lower critical solution temperature [1].

The goal of this report is to provide practical guidance, in terms of solubility, for people intending to make coatings from the copolymers as well as those intent on solution characterization. Fractionation via extraction could be used to determine comonomer concentration distribution. Techniques such as size exclusion chromatography (molecular weight distribution), light scattering (weight-average molecular weight, M_w), and vapor phase osmometry (number-average molecular weight) might also be employed.

EXPERIMENTAL

A poly(tetrafluoroethylene) (PTFE) sample and five HFP copolymers were analyzed. The PTFE, PTFE-6, is described in a previous reference to have a $\overline{M}_w$ of 340,000 [2]. A high melting copolymer was previously found to have a $\overline{M}_w$ of 241,000 and is referred to as FEP-1 [3]. Four lower melting copolymers were supplied by Dr. Richard A. Morgan of the DuPont Company. They were synthesized by the normal aqueous free-radical dispersion method, but with higher HFP content than FEP-1, and have been designated as LMFEP. Although a detailed molecular weight analysis was not performed on the LMFEP, their low shear rate viscosities indicate that they have $\overline{M}_w$ in the vicinity of 1.2×10^5, 2.1×10^5 and 1.5×10^5 for LMFEP-1, 2 and 3, respectively. These calculations assumed that the viscosity was proportional to the 3.4 power of $\overline{M}_w$. Table I is a list of all the polymers with their HFP contents and low shear rate melt viscosities. HFP content was determined by Morgan using an infrared technique calibrated with ^{19}F NMR. The ratio of the infrared absorptions at 983/2357 cm^{-1} were multiplied by about 3.1 to get weight % HFP. The sample designated LMFEP-2 was polymerized in commercial quantities. The other LMFEP samples were prepared on a semi-works scale by Morgan. The sample designated LMFEP-1F is sample LMFEP-1 which has been post-treated with elemental fluorine to reduce the acid end-group concentration from 1010 to 110 ppm. Acid ends are always obtained with the type of polymerizations employed for these polymers.

DSC (differential scanning calorimetry) analysis was performed by Howard Starkweather (DuPont Experimental Station) to assess differences in melting behavior and attempt to correlate this with dissolution behavior. Approximately 10 mg samples were heated at 10°C/min in a Dupont Instruments 910 DSC. The following data were obtained in the heating mode following a "quench" cooling from the melt. Figure 1 compares the melting behavior of PTFE, FEP and a representative sample of LMFEP. As expected, increasing the HFP content broadens and lowers the melting range as well as lowering the degree of crystallinity. Table II lists some aspects of the DSC behavior for each polymer. The start, finish and peak of the melting endotherm are listed with the heat of fusion (ΔH_U), the latter being proportional to the degree of crystallinity.

Most of the dissolution experiments were carried out in 8 mm sealed glass tubes. Temperature control was obtained by placing these tubes in aluminum heating blocks fitted with viewing ports for visually observing the dissolution process. This was a convenient experimental procedure because the lower boiling $C_{14}F_{24}$ could be confined and used

TABLE I

Polymer Description

Sample	Mole % HFP	Melt Viscosity (Pa · s × 10^{-3})
PTFE-6	0.0	2.6[a]
FEP-1	9.2	2.0[b]
LMFEP-1	18.2	0.2[b]
LMFEP-1F	18.2	0.2[b]
LMFEP-2	19.3	1.2[b]
LMFEP-3	18.0	0.38[b]

[a]Zero shear viscosity, measured at 380°C by creep and oscillatory shear.
[b]Shear viscosity measured at 372°C, 4.48 × 10^4 Pa shear stress in a melt indexer.
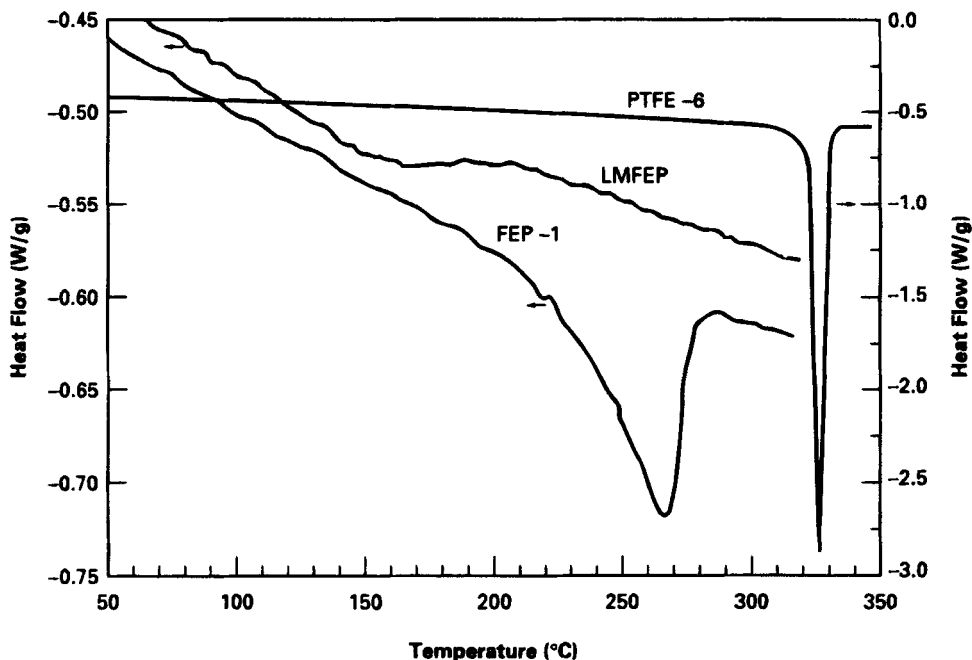
FIGURE 1   DSC traces for PTFE-6, FEP-1, and a representative sample of LMFEP (sample 2). The FEP-1 and LMFEP-2 are plotted on a more sensitive heat flow axis due to the large difference in their melting endotherms versus PTFE.

TABLE II

DSC Data

Sample	Start (°C)	Finish (°C)	Peak (°C)	ΔHU (J/g)
PTFE-6	300	330	326	70.3
FEP-1	175	285	265	25.3
LMFEP-1	92	210	148	9.0
LMFEP-1F	90	210	147	9.6
LMFEP-2	60	200	147	11.1
LMFEP-3	80	205	166	11.2

to dissolve PTFE at more than 50°C above its boiling point. Thus comparative dissolution behavior could be studied in the same solvent. The temperature (T_D), at which complete dissolution occurred, the temperature (T_C), at which recrystallization occurred on cooling, and the solution melting point (T_M), at which complete dissolution occurred on reheating, were recorded. The equipment and procedures were previously described in greater detail [1]. For the homopolymer (PTFE), T_M and T_C can be determined within a few degrees because an easy-to-observe turbidity disappears or develops at T_M and T_C, respectively. With the copolymers, however, the solutions usually remain transparent upon cooling. T_C and T_M were thus more qualitatively gauged by observing the temperature at which large viscosity increases (T_C) or decreases (T_M) were observed.

The solvents were used as-received except for perfloroeicosane whose purification has been previously described [1]. They are listed in Table III with their normal boiling points and molar volumes. Flutec® PP25 ($C_{17}F_{30}$) is a mixture of the isomers of perfluoromethylcyclohexyldecalin. It has a boiling range of approximately 250 to 260°C. PP25 was most easily obtained in this country as Fluorinert® FC-71, marketed by the 3M Corporation. Flutec® is a tradename for perfluorocarbon liquids now sold by British Nuclear Fuels Ltd., Preston, Lancashire, UK.

RESULTS AND DISCUSSION

1. Effect of HFP Content

Table IV summarizes the dissolution, recrystallization and melting behavior for 5% solutions of the polymers as a function of HFP content. All experiments were performed in $C_{14}F_{24}$ except for FEP-1 where $C_{17}F_{30}$ was the solvent. As expected, solubility generally increases with increasing HFP concentration. This is because polymer crystallinity, as

TABLE III

Solvents

Chemical Name	Formula	Trade-name	Supplier	Boil. Pt.(°C)	$\bar{V}_P$
perfluoro-n-pentane	n-C_5F_{12}	Flutec® PP50	PCR (Gainesville, FL, USA)	29	173
perfluoro-octane	n-C_8F_{18}	—	—	100	253
perfluoro-n-eicosane	n-$C_{20}F_{42}$	—	—	300	577[b]
hexafluoro-benzene	C_6F_6	—	Aldrich (Milwaukee, WI, USA)	80	115[c]
perfluoromethyl-cyclohexane	C_7F_{14}	Flutec® PP2	PCR	76	197
perfluoro-decalin	$C_{10}F_{18}$	Flutec® PP6	PCR	142	242
perfluoro-tetradecahydro-phenanthrene	$C_{14}F_{24}$	Flutec® PP11	PCR	215	307
perfluoro-methylcyclohexyl-decalin	$C_{17}F_{30}$	Flutec® PP25	3M (St. Paul, MN, USA)	250–260	378[c]
hexafluoro-propylene oxide oligomer	$(C_3F_6O)_n$	Krytox® 16350	Dupont (Wilmington, DE, USA)	>300	—
chloro-trifluoroethylene-oligomer	$(C_2ClF_3)_n$	Fluorolube® LG-160	Occidental (Niagara Falls. NY, USA)	>300	—

[a]molar volume in cm³/mole calculated at 20°C from manufacturer's data.

[b]estimated based on the density of n-perfluorononane at 20°C; n-perfluoroeicosane is a solid with melting point well above room temperature.

[c]calculated at 25°C

TABLE IV

Effect of HFP Content on Solution Behavior in $C_{14}F_{24}$

Sample	% HFP	$T_D(°C)$	$T_C(°C)$[a]	$T_M(°C)$[a]
PTFE-6	0.0	285–290	255–260	275–280
FEP-1	9.2	253	180[b]	200[b]
(in $C_{17}F_{30}$)				
LMFEP-1	18.2	110–120	80–85[c]	110–120[c]
LMFEP-2	19.3	160	90–95[c]	122–128[c]
LMFEP-3	18.0	135	85–90[c]	115–120[c]

[a]Viscosity gradually increased on cooling for all the FEP solutions and decreased on heating. T_C reflects immobility and T_M the end of drastic decreases.
[b]Viscosity changes observed by rheological measurements (see Figure 2).
[c]Viscosity changes observed visually, only.

well as the melting and crystallization temperatures, decreases with increasing HFP. The increased solubility is reflected in the lower dissolution temperatures and broader temperature ranges over which solution stability is observed. LMFEP-2 (which has the highest HFP concentration) was observed to have slightly higher dissolution, crystallization and melting temperatures than LMFEP-1 and 3. This can probably be explained by differences in HFP distribution, uncertainty in the temperature determinations of about 3°C and/or uncertainty in the HFP concentration determinations. As could have been predicted from the data in Table IV, the lower boiling $C_{14}F_{24}$ is an excellent ambient pressure solvent for LMFEP and $C_{17}F_{30}$ easily dissolves FEP-1 at ambient pressure.

As HFP increases, it gets more difficult to determine a precise melting (T_M) and recrystallization temperature (T_C). For PTFE, an easily observed turbidity develops and disappears at T_C and T_M, respectively. With FEP the turbidity is more difficult to observe but a determination of the viscosity as a function of increasing and decreasing temperature allows a more quantitative assessment of melting and recrystallization. Figure 2 is a plot of the viscosity of a 5% FEP-1 solution in Flutec® PP25 ($C_{17}F_{30}$). From these data, we determined T_M and T_C to be about 200° and 180°C, respectively. We visually observed viscosity changes to be more gradual with LMFEP solutions. (Visual observations involved watching the ease of flow upon picking up the heating chambers and turning them from side-to-side.)

2. Effect of End Groups

The fluorinated version of LMFEP-1 (LMFEP-1F) shows surprisingly higher dissolution, recrystallization and melting temperatures than its unfluorinated counterpart when dissolved in $C_{14}F_{24}$. (This behavior was not observed when hexafluorobenzene was used as the solvent; this is discussed later in this paper.) These data are summarized in Table V for 5% solutions. An initial explanation would seem to be that the fluorination has reduced the number of bulky acid end groups which inhibit polymer crystallization. Thus, fluorinated polymer should show a higher melting range and greater crystallinity. The DSC scans are not significantly different for LMFEP-1 and LMFEP-1F, however, as reflected by the data in Table II.

Another possible explanation is that dissolution somehow changes the polymer in a way different than the melting of undiluted polymer. DSC of dried samples of each of these
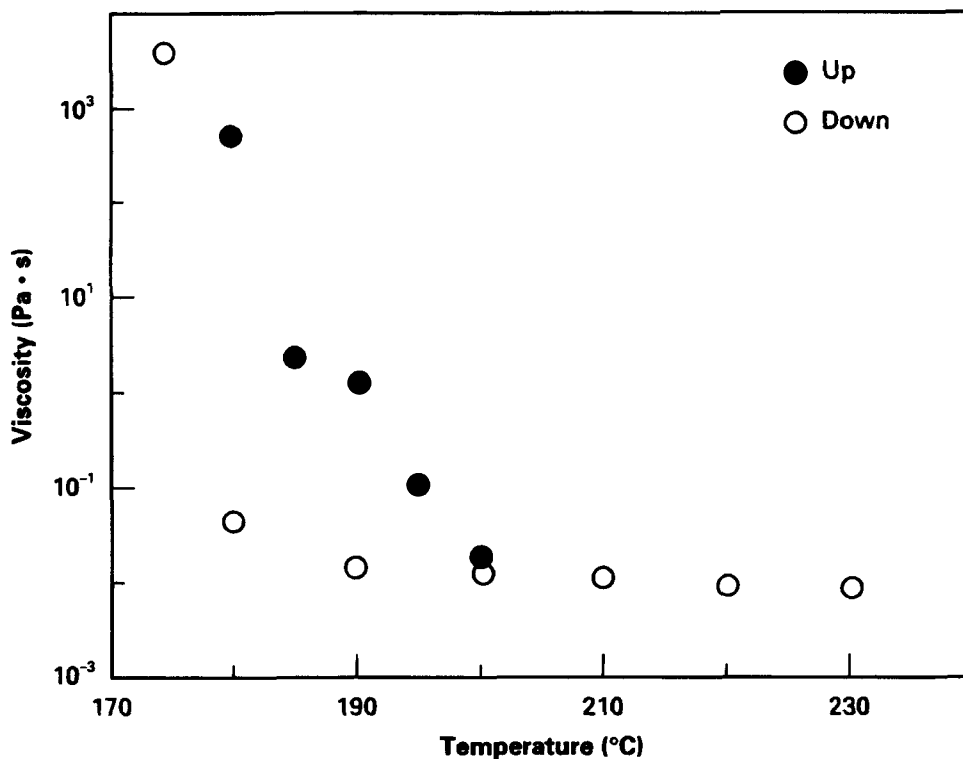
FIGURE 2   Viscosity as a function of temperature for a 5% solution of FEP-1 in $C_{17}F_{30}$. The viscosity was measured in a Bohlin constant stress rheometer at 0.2 Pa shear stress. "Up" and "Down" in the legend refers to increasing and decreasing temperature, respectively.

TABLE V

Effect of Fluorination on the Solubility of LMFEP

Sample	$T_D(°C)$	$T_C(°C)$	$T_M(°C)$
LMFEP-1	118	90–100	110
LMFEP-1F	160–165	155	160–165

polymers was not significantly different than the behavior seen on "never-dissolved" polymer. We currently have no explanation for the poorer solubility of fluorinated polymer.

3. Effect of Polymer Concentration

The effects of varying polymer concentration were studied for both FEP-1 and LMFEP-1. Tables VI and VII summarize the findings. For FEP-1 in Table VI, visual observations were made at 1% concentration in $C_{14}F_{24}$ using the sealed glass tubes. At 5% concentration, solutions were made at atmospheric pressure in $C_{17}F_{30}$ at about 253°C and melting and crystallization temperatures were determined from viscosity measurements as described above. Considering the differences in the observational techniques, the results

TABLE VI

Solubility Versus FEP-1 Concentration

% Polymer	$T_D(°C)$	$T_C(°C)$	$T_M(°C)$
1.0	246	190	205–210[a]
5.0	253	180	200[b]

[a]Visual Observations in $C_{14}F_{24}$
[b]Viscosity measurements in $C_{17}F_{30}$

TABLE VII

Solubility Versus LMFEP Concentration

% Polymer	$T_D(°C)$	$T_C(°C)$	$T_M(°C)$
1.0	105	45–50	87
5.0	110–120	85	103
10.0	130	110	120

are not significantly different. Since the $C_{17}F_{30}$ has a higher molar volume than $C_{14}F_{24}$, the observed melting and crystallization temperatures in Table VI are suspected to be slightly higher for the 5% solution than if $C_{14}F_{24}$ were used.

The measurements recorded in Table VII for LMFEP-1 were the result of visual observations in sealed glass tubes using $C_{14}F_{24}$ as solvent. Unlike FEP-1, which has lower HFP content, there appears to be a tendency towards greater solubility with decreasing polymer concentration.

4. Effect of Varying the Solvent

The effects of different solvents are summarized in Tables VIII and IX. Dissolution experiments for 1% concentration of FEP-1 were tried with $C_{14}F_{24}$, perfluoroeicosane (n-$C_{20}F_{42}$), Krytox®, and Fluorolube®. The results are in Table VIII. The more polar solvents, Krytox® and Fluorolube®, raised the solution melting point (reported in this case as T_D). Since FEP is at least as non-polar as PTFE[4] and the solubility of PTFE is dominated by entropy effects, it is not surprising that a polar solvent raises the melting temperature of the solution. This same effect was observed for PTFE [1]. As noted in Table VIII, the samples swelled but did not dissolve in Krytox® or Fluorolube® after 24 hours. It is expected that given sufficient time, Fluorolube® would have dissolved the FEP sample, since it is a solvent for PTFE [5]. The Krytox® would not be expected to dissolve the FEP sample, however, since it is not a solvent for PTFE [1].

As was observed with PTFE [1], cyclic perfluoroalkanes are more effective solvents than the non-cyclic ones. The higher T_D, T_C, and T_M for the n-$C_{20}F_{42}$ versus the $C_{14}F_{24}$ solutions exemplifies this. Higher density and/or lower molar volume for the cyclic compounds at similar boiling points appears to be the explanation for their superior solvating power [1].

As stated previously, more stable (lower T_D, T_C, and T_M) solutions will occur with solvents which minimize molar volume. The minimum liquid molar volume (approximated by the values given in Table III at room temperature) increases with molecular weight in

TABLE VIII

Solubility of 1% FEP-1 in Different Solvents

Solvent	$T_D(°C)$	$T_C(°C)$	$T_M(°C)$
$C_{14}F_{24}$	246	190	205–210
$n-C_{20}F_{42}$	260	220–225	250
Fluorolube®	270[a]	—	—
Krytox®	300[a]	—	—

[a]Swollen but not dissolved after 24 hours.

TABLE IX

Solubility of 5% LMFEP-1 in Different Solvents

Solvent	$T_D(°C)$	$T_C(°C)$	$T_M(°C)$	$T_{CRIT}(°C)$
C_6F_6	85–90	75	88	244[a]
C_7F_{14}	155	115	155	213[b]
$C_{10}F_{18}$	100–125	75–100	100–125	292[b]
$C_{14}F_{24}$	115	80	113	377[b]

[a]Reference 6.
[b]British Nuclear Fuels, Ltd. product literature.

a homologous series. However, if external pressure is not applied, a solvent's molar volume (at the dissolution temperature) will increase dramatically as the dissolution temperature approaches the solvent's critical temperature (T_{CRIT}). Also, T_{CRIT} increases with molecular weight in a homologous series. At the nearly constant pressure that exists in our sealed tubes, one would expect molar volume at the dissolution temperature (and thus T_D, T_C, and T_M) to reach a minimum value with increasing molecular weight. The optimum molecular size for obtaining the widest solubility range with aliphatic, cyclic perfluorinated solvents for LMFEP appears to lie between that of $C_{10}F_{18}$ and $C_{14}F_{24}$ based on the data presented in Table IX for the bottom three solvents. T_{CRIT} for each solvent is also listed in Table IX; values were taken from the British Nuclear Fuels, Ltd product literature.

Perfluorobenzene appears to be the best solvent for LMFEP if contained in a sealed container (Table IX). It would not be expected to dissolve the polymer at reflux (80°C). However, if dissolved in a sealed container, a 5% solution would be expected to be stable at atmospheric pressure below the solvent's boiling point. The low molar volume of perfluorobenzene in combination with its relatively high T_{CRIT} of 244°C [6] could be one explanation for its greater solvent power versus the other liquids listed in Table IX. However, perfluorobenzene is more polar than these other solvents and one could argue that the high level of acid ends in LMFEP-1 increases this polymer's polarity to get a fortuitous enthalpic interaction. If this were true, the less polar fluorinated sample, LMFEP-1F, should have much higher values for T_D, T_C, and T_M. We have experimentally determined that there is no significant difference between the solubility characteristics of the fluorinated or unfluorinated samples in perfluorobenzene. This is surprising since, as mentioned in Section 2, the fluorinated sample dissolved at much higher temperatures in $C_{14}F_{24}$. Thus, perfluorobenzene's low molar volume at high T_{CRIT} appears to be the reason for its excellent solvency of LMFEP.

We attempted to dissolve LMFEP-1 in the low boiling, liquid perfluoroalkanes, perfluoro-n-pentane and perfluorooctane. Only partial solubility resulted. The polymer sample

swelled in both solvents at 150° to 160°C but did not dissolve. On cooling to room temperature, an opaque, polymer-rich layer occupied the bottom of the tubes occupying about 10–15% of the volume of the tube contents. The top layer was cloudy for the pentane and contained a feathery, solid material in the case of the octane. It is thus concluded that partial solubility occurred. These solvents have relatively high liquid molar volumes with low T_{CRIT} (148° and 200°C for n-C_5F_{12} and C_8F_{18}, respectively [7]) when compared to cyclic perfluorocarbons. This will lead to relatively high solvent molar volumes at the dissolution temperatures and in turn could result in the lower critical solution temperature being slightly lower than the solution melting temperature. The observed partial solubility is consistent with this explanation. Similar effects were observed with PTFE solubility [1].

Extracting with these lower boiling linear perfluoroalkanes plus perfluorobenzene, as well as different chlorofluorocarbons such as CCl_2FCClF_2(bp = 46°C), $CFCl_3$(bp = 248C), or Fluorinert® FC-75 (a perfluorinated ether boiling at 102°C sold by the 3M Corporation) might be a route to fractionation of this polymer. These latter solvents were shown to dissolve PTFE when external pressure was applied to the system [8]. Subsequent characterization of the eluted fractions could lead to an understanding of the molecular weight and comonomer composition distributions.

Acknowledgements

References

1. W. H. Tuminello and G. T. Dee, *Macromolecules*, 2, 699 (1994).
2. W. H. Tuminello, T. A. Treat, and A. D. English, *Macromolecules*, 21, 2606 (1988).
3. W. H. Tuminello, *Polym. Eng. Sci.*, 29, 645 (1989).
4. H. W. Starkweather, *Macromolecules*, 10, 1161 (1977).
5. B. Chu, C. Wu and W. Buck, *Macromolecules*, 21, 397 (1988).
6. R. C. Reid, J. M. Prausnitz and B. E. Poling, *The Properties of Liquids and Gases*, 4th Edition, McGraw-Hill, USA (1987).
7. P. Smith and K. H. Gardner, *Macromolecules*, 18, 1222 (1985).
8. W. H. Tuminello, D. J. Brill, D. J. Walsh and M. E. Paulaitis, *J. Appl. Polym. Sci.*, 56, 495 (1995).