Solid-State NMR Characterization of Motion in Flexible Polyurethane Foams

J. C. MORELAND,[1,*] G. L. WILKES,[1,†] C. G. MORELAND,[2] S. S. SANKAR,[2] E. O. STEJSKAL,[2] and R. B. TURNER[3]

[1]Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute & State University, Blacksburg, Virginia 24061-0211, [2]Department of Chemistry, North Carolina State University, Raleigh, North Carolina, and [3]Polyurethanes Products Research, Dow Chemical Company, Freeport, Texas 77541

SYNOPSIS

High-resolution solid-state ^{13}C-NMR has been used to study the phase separation and molecular motion in two series of polyurethane foams. These two series differ by one possessing the additive of lithium chloride, LiCl. NMR relaxation times can map the motion throughout the polymer molecule and detect changes in that motion arising from either microseparation or phase mixing between the different segments. There are only slight changes in the soft segment $T_{1\rho}$(^{13}C) values as well as an increase in the hard segment $T_{1\rho}$(^{1}H) values with increase in the hard segment content for the foams studied. The $T_{1\rho}$(^{1}H) and $T_{1\rho}$(^{13}C) values do indicate that the phase separation of the hard and soft segments is similar for all foams. A decrease in the $T_{1\rho}$(^{1}H) and $T_{1\rho}$(^{13}C) values with increasing LiCl content indicates that the motion of the soft segments is restricted more by the hard segments. This is explained by more phase mixing in the foams containing the LiCl additive. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Structure–property relationships in polymers are evaluated to obtain a better understanding of the resulting morphology and its relationship to the mechanical and related properties. Previously, we reported on the morphological features of the micro- and macrostructural features of the solid portion of flexible water-blown polyurethane foams where detailed composition has been provided elsewhere.[1] The two principal components, however, are based on glycerin-extended polypropylene oxide and water-extended toluene diisocyanate 80 : 20 mixture of 2,4 and 2,6 isomers, respectively.[1–4] In one of these studies, a systematic series of four slabstock polyurethane foams designated as F1–F4, which varied in hard segment content (21–34 wt %) were characterized by using several morphological and structural techniques.[1–3] Small-angle X-ray scattering

(SAXS) and dynamic mechanical spectroscopy (DMS) established that these foams had a two-phase morphology that is somewhat similar to that of urethane and urea–urethane elastomers. Transmission electron microscopy (TEM) results showed evidence of urea-based aggregates that increased in content and somewhat in size with increasing hard segment content. In another previous study, the effect of adding lithium chloride (LiCl) to the formulation of flexible slabstock polyurethane foams (44-0, 44-4, and 44-5) was also analyzed.[4] This latter study revealed that distinct structural changes in the solid portion of the foam took place that were believed to be principally related to the breakup of the urea aggregate structures due to the presence of the LiCl additives, which helps solubilize the urea-based segments. These changes suggested that smaller aggregate structures were formed and/or the hard segments were better dispersed within the network structure upon adding LiCl to the formulation.

High-resolution solid-state ^{13}C-NMR has been used to study the phase separation, aggregation, and molecular motion in several polymers.[5–11] The cross polarization (CP) procedure used to obtain the solid

---

state ^{13}C-NMR spectra involves manipulation of proton and carbon spin polarizations along the rotating radiofrequency field. These manipulations depend on several rotating frame relaxation times, most often $T_{1\rho}(^1H)$ and $T_{1\rho}(^{13}C)$ that are sensitive to lower frequency motions (from a few kilohertz to a few hundred kilohertz). These relaxation times can map the motion throughout the polymer molecule and detect changes in that motion arising from either microseparation or phase mixing between the different segments. Within this study, results obtained from these relaxation experiments are given for the above-mentioned polyurethane foams, which varied in both hard segment as well as in LiCl concentration. The objective of this work was to provide further evidence on the structural features of these foams that vary in their specific chemical formulations.

EXPERIMENTAL

The solid-state ^{13}C-NMR spectra were obtained under matched Hartmann–Hahn conditions around 50 kHz on a Chemageitics CMC 200S NMR spectrometer equipped with a CP-MAS probe. The pulse sequences employed in this study are shown in Figure
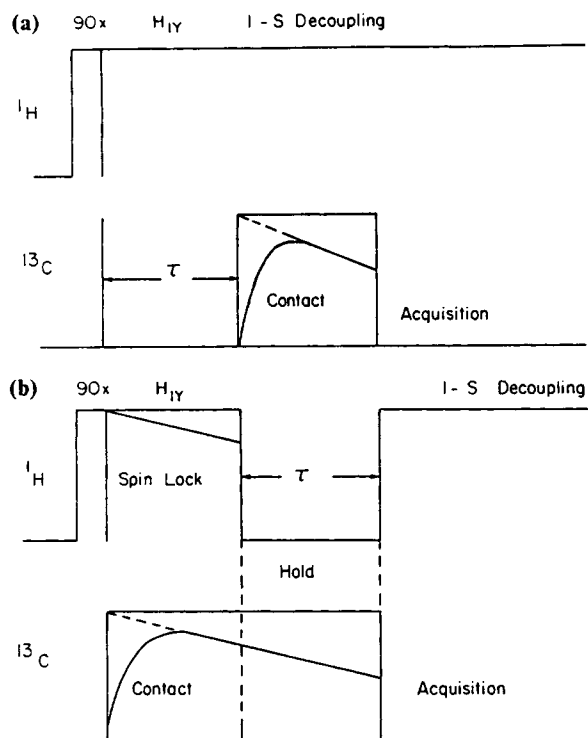

Figure 1 Pulse sequence for (a) $T_{1\rho}(^{13}C)$ and (b) $T_{1\rho}(^1H)$ relaxation times.

Table I   Composition and Density of Foams

Foam	pphp H_2O*	LiCl Content (pphp)[a]	Density (lb/ft^3)	Wt % HS
F1	2	—	2.85	21.1
F2	3	—	1.92	25.8
F3	4	—	1.43	30.1
F4	5	—	1.24	33.8
44-0	5	0.0	1.36	33.8
44-4	5	0.4	1.43	33.8
44-5	5	0.5	1.51	33.8

[a] pphp = parts by weight per hundred parts by weight of polypropylene oxide soft segment material.

1. For the $T_{1\rho}$ measurements, 2000 transients (block-averaged in groups of 200) were collected for each τ value over a spectral width of 15 kHz using 2K data points, a 5.2-μs 90° pulse, and with a spinning rate of approximately 4 kHz. The relaxation times were determined by fitting the experimental data to several model distributions of first-order relaxation behavior by means of a PC-XT program, RE-LAX(tion), written by Robert Skarjune, 3M Corp.

The polyurethane foams utilized in this study were foams designated F1, F2, F3, F4, 44-0, 44-4, and 44-5. As stated earlier, the first four of these foams, F1–F4, as well as the latter series of three had been structurally investigated along with their viscoelastic behavior and reported upon in previous but separate publications.[2,4] A summary of important composition information is given in Table I for these materials. A typical ^{13}C spectrum for these foams is shown in Figure 2 by using F3. The corresponding chemical shift assignments are given in Table II. The carbon assignments are shown in Figure 3 for the chemical structures of the soft and hard segments. In the discussion, the 130–131 ppm chemical shift is associated with the hard segments and the 73 ppm chemical shift is affiliated with the polypropylene oxide soft segments.

RESULTS AND DISCUSSION

In Figure 4 the $T_{1\rho}(^1H)$ relaxation times for the hard and soft segments are shown as a function of hard segment content. These values given in Figure 4 as well as the $T_{1\rho}(^1H)$ values for the other carbons are summarized in Table III. As shown, the values of $T_{1\rho}(^1H)$ for the soft segments, obtained from the peak at ca. 131 ppm, are rather independent of composition. On the other hand, the $T_{1\rho}(^1H)$ values for
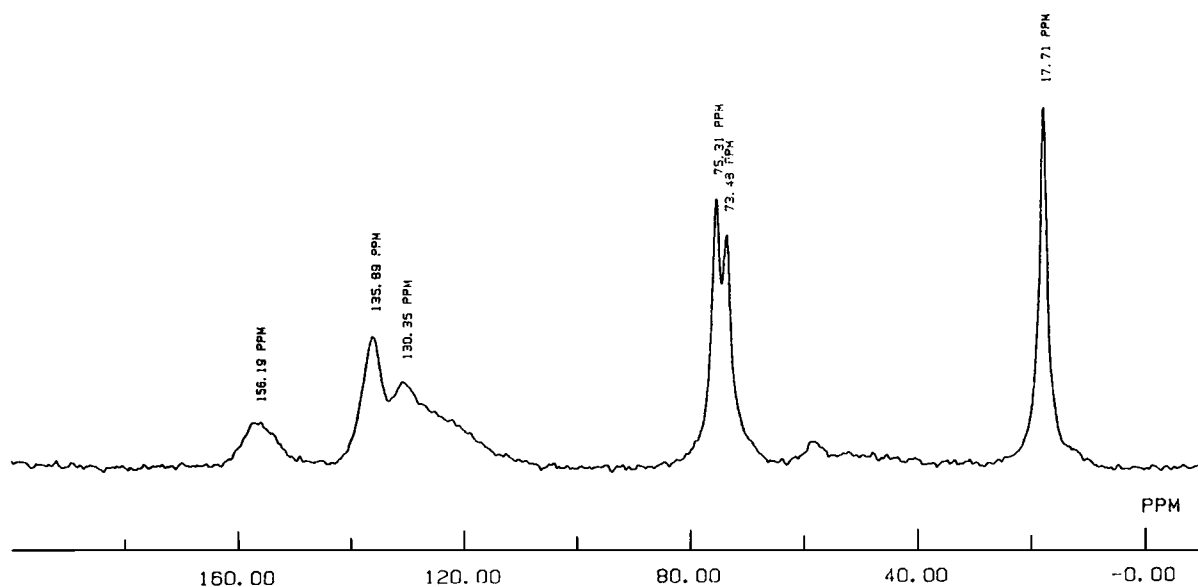
Figure 2   Solid-state ^{13}C-NMR spectrum for foam F3.

the hard segments (ca. 73 ppm) do increase systematically with increasing hard segment content. The values of $T_{1\rho}(^1H)$ for the hard and soft segments of foams 44-0, 44-4, and 44-5 are shown as a function of LiCl content in Figure 5. All of the $T_{1\rho}(^1H)$ values obtained for this latter series are also summarized in Table IV. As shown in Figure 5, there is a steady decrease in both the hard and soft values of $T_{1\rho}(^1H)$ values with increasing LiCl content.

The proton $T_{1\rho}$'s are influenced by spin diffusion due to the presence of strongly coupled protons. Spin diffusion causes the $T_{1\rho}(^1H)$ to be the same for all protons, *even if observed* through different carbons, in a homogenously dispersed system. The proton $T_{1\rho}$'s of a segmental system are strongly dependent on the short-range spatial proximity, or mixing, of various components. For foams F1–F4 where hard segment content increases, respectively, from 21 to 34 wt %, there is an increase in the interfacial region

of the hard and soft segments from 0.7 to 1.6 nm with increasing hard segment content as determined earlier by SAXS.[2] Therefore, it was initially expected to see changes in the values of $T_{1\rho}(^1H)$ for the soft and hard segments with composition. If the thickness of the interface region is significant, a decrease in the difference between the hard and soft segment values of $T_{1\rho}(^1H)$ values with increasing hard segment content would be expected. However, as shown in Figure 4 the values of $T_{1\rho}(^1H)$ obtained for foams F1–F4 do not agree with this argument—in fact these values exhibit the opposite trend. A possible explanation for this is due to an increase in the *size* of the urea aggregate structures with increasing hard segment content for foams F1–F4. With the larger aggregate structure present, the influence of spin diffusion from the soft segment to the hard segment is reduced based on the greater distances over which spin diffusion can occur. In an attempt to confirm

Table II   Chemical Shift Assignments (in conjunction with Fig. 3)

Carbon #	Chemical Shift (ppm)	Segmental Representation
C-8	156	Hard
C-2, C-4 (2, 4 TD)	136	Hard
C-2, C-6 (2, 6 TDI)	136	Hard
C-1, protonated aromatic carbons	131	Hard
C-10	75	Soft
C-9	73	Soft
C-7, C-11	18	Hard, soft

Soft Segment

$$CH_2 - O - (- CH_2 - \underset{10}{CH} - O -)_x - H$$
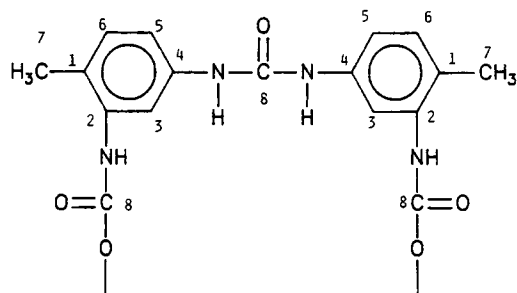$$\underset{9}{} \quad \underset{10}{\overset{\overset{\displaystyle CH_3}{|}}{}}$$
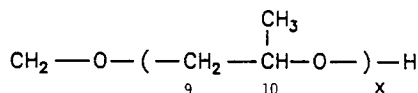
Hard Segment

Figure 3 Basic repeat units for the glycerin-extended polypropylene oxide soft segment and polyurea hard segment based on water-extended TDI.

Figure 4 Effect of hard segment content on the values of $T_{1\rho}(^1H)$ (131 ppm represents the hard segment and 73 ppm represents soft segment; see Table II for more details).

this speculation, $T_{1\rho}(^1H)$ measurements were also made on the second series of foams 44-0, 44-4, and 44-5 where the index level was 100 versus 110 for the prior series but more importantly, the latter two members of the series contained the LiCl additive.

The results given in Figure 5 show that a decrease is observed for the hard and soft segment $T_{1\rho}(^1H)$ values obtained from foams 44-0, 44-4, and 44-5. This decrease is believed due to the influence of spin diffusion between the two segments, which increases with LiCl content. This explanation does seem plausible based on the morphological changes, i.e., reduction and/or removal of the large aggregate structures that is believed to take place upon the addition of LiCl to the formulation, as discussed in a previous study.[4] Such changes allow for spin diffusion to be more effective between the soft and hard segments. Another possible explanation is that the
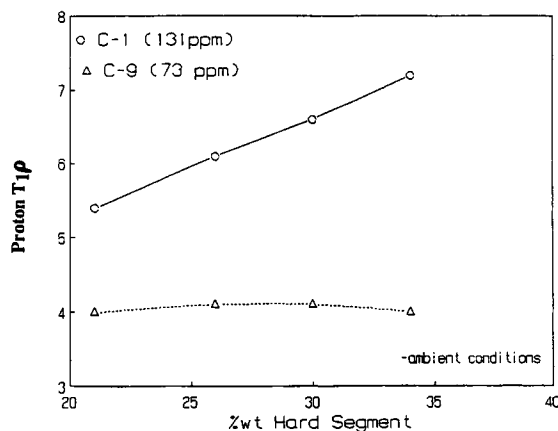
motion of the soft segments is more restricted by the hard segments with increasing LiCl content. Alternatively, the hard segments may be becoming more mobile or the domains in which they reside are less cohesive or rigid. These changes in the segmental mobility with increasing LiCl content are thought to occur (as discussed in detail in our previous study) due to more phase mixing in foams 44-5 versus 44.0. This has been indicated by the slightly higher soft segment glass transition temperature obtained from differential scanning calorimetry (DSC) measurements as well as less distinct polyurea aggregate structures observed in foam 44-5 by TEM in comparison to foam 44-0.[4]

This latter explanation does assume that the soft segment $T_{1\rho}(^1H)$ values are on the high-frequency side or high-temperature side of $T_{1\rho}(^1H)$ minimum, whereas the hard segment $T_{1\rho}(^1H)$ values are on the low-frequency side. In an attempt to confirm this assumption, $T_{1\rho}(^1H)$ measurements were made at 45°C. The soft segment $T_{1\rho}(^1H)$ values increased

Table III   Proton $T_{1\rho}$ (ms)[a] Values at Ambient Conditions for Foams F1-F4[b]

Foam	Wt % HS[c]	18 ppm	73 ppm	75 ppm	131 ppm	136 ppm	156 ppm
F1	21.1	6.4	4.0	4.3	5.4	5.1	6.3
F2	25.8	6.0	4.1	4.6	6.1	5.7	6.9
F3	30.1	5.7	4.1	4.4	6.6	6.2	7.1
F4	33.8	6.1	4.0	4.6	7.2	6.9	6.9

[a] Error in $T_{1\rho}$ (^1H) values are ± 0.3 ms.
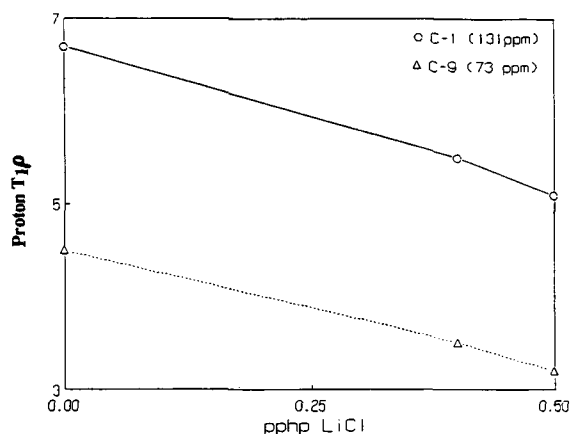[b] The band assignments are given in Table I and Figure 2.
[c] HS = hard segment.

Figure 5   Effect of LiCl content on values of $T_{1\rho}(^1H)$ (131 ppm represents hard segment and 73 ppm represents soft segment; see Table II for more details).

with increasing temperature; thus demonstrating that the motion of the soft segments are fairly rapid and therefore on the high-temperature side. On the other hand, the hard segment values showed very little change with increasing temperature; therefore indicating that the hard segment values are at or near the minimum of the $T_{1\rho}(^1H)$ inverse temperature curve. In addition, this small change may suggest that this minimum for the hard segment $T_{1\rho}(^1H)$ values is fairly broad. For a polyurethane-based network, Dickenson et al. have also shown similar behavior for $T_{1\rho}(^1H)$ values for the soft segments and for $T_{1\rho}(^{13}C)$ values for the hard segments.[12] Thus, the high-temperature results do indicate that the mobility of the soft segments is being effected with increasing LiCl content for the reasons suggested above. On the other hand, it appears that the decrease in the hard segment $T_{1\rho}(^1H)$ values is influenced mostly by spin diffusion and not by changes in the mobility of the hard segments since the $T_{1\rho}(^1H)$ values show very little dependence on temperature near ambient conditions. This dependence does indicate that the reduction and/or removal of the large urea aggregate structures is caus-

ing the majority of the decrease in the hard segment $T_{1\rho}(^1H)$ values with increasing LiCl content. In addition, since this series of foams (44-0, 44-4, and 44-5) has a constant hard segment content, the behavior of their hard segment $T_{1\rho}(^1H)$ values gives further support to the above speculation for foams F1–F4. That is, the polyurea aggregate structure for foams F1–F4 whose content varies as F4 > F3 > F2 > F1 is causing an increase in the values of $T_{1\rho}(^1H)$ with increasing hard segment content. In the following paragraph, the topic of mobility is addressed further through discussion of the $T_{1\rho}(^{13}C)$ values.

The $T_{1\rho}(^{13}C)$ results have only been obtained for foams F1, F3, 44-0, and 44-5 and are summarized in Table V. $T_{1\rho}(^{13}C)$ values are shown for carbons representing both the soft and hard segments, but the values for the soft segment carbons are only considered here due to the lack of significant mobility in the hard segments. Furthermore, the $T_{1\rho}(^{13}C)$ values are a measure of the *localized motion* since ^{13}C is not that abundant and *cannot be influenced by spin diffusion*.

As shown in Table V, the soft segment $T_{1\rho}(^{13}C)$ values for F1 and F3 do appear to increase slightly, but not within experimental error, with increasing hard segment content. Therefore, this relatively insignificant change in the values for F1–F3 would indicate that increasing hard segment content has little effect on the motion of the soft segment. For foams 44-0 and 44-5, there is a rather significant decrease in the $T_{1\rho}(^{13}C)$ values for the soft segments with increasing LiCl content (see Table V). This decrease indicates that the *motion of soft segments in foam 44-5 is distinctly less than that of foam 44-0*. As suggested above, the reduction in the mobility of the soft segments of foam 44-5 is believed to be brought about by the hard segments restricting the motion of the soft segments due to higher level of segmental mixing. The difference in the mobility of the soft segments in these two foams is believed to be related to the changes that occur in the morphological features upon addition of LiCl to the formulation of foam 44-5. As discussed in our previous

Table IV   Proton $T_{1\rho}$ (ms)[a] Values at Ambient Conditions Foams for 44-(0–5)[b]

Foam	pphp LiCl	18 ppm	73 ppm	75 ppm	131 ppm	136 ppm	156 ppm
F44-0	0	6.5	4.5	4.7	6.6	6.5	7.2
F44-4	0.4	5.0	3.5	3.6	5.5	5.5	5.2
F44-5	0.5	4.7	3.2	3.3	5.1	4.8	5.4

[a] Error in $T_{1\rho}$ (^1H) values are ± 0.3 ms.
[b] The band assignments are given in Table I and Figure 2.

Table V   Carbon $T_{1\rho}$ (ms)[a] Values at Ambient Conditions[b]

Foam	Wt % HS[c]	pphp LiCl	18 ppm	73 ppm	75 ppm	131 ppm
F1	21.1	0	23.2	8.1	8.5	(24)
F3	30.1	0	24.0	8.5	9.1	(43)
44-0	34	0	28.7	9.6	10.3	(56)
44-5	34	0.5	19	6.4	6.9	(48)

[a] Error in $T_{1\rho}$ (^{13}C) is ± 0.3 ms.

[b] The band assignments are given in Table I and Figure 2. Values in parentheses are inaccurate due to long relaxation times in hard segments.

[c] HS = hard segment.

study, these changes are believed to result in a better dispersion of the hard segments and/or formation of smaller aggregate structures within the network structure of the foam.[4]

CONCLUDING REMARKS

From the results for the soft segment $T_{1\rho}(^1\mathrm{C})$ values of foams F1–F4 and the $T_{1\rho}(^1\mathrm{H})$ values for all of the foams studied, it can be concluded that the majority of the increase in the hard segment $T_{1\rho}(^1\mathrm{H})$ values with hard segment content is due to the increase in the size and rigidity of the polyurea aggregate structures in these foams. Based on the rather small change in the soft segment $T_{1\rho}(^1\mathrm{H})$ and $T_{1\rho}(^{13}\mathrm{C})$ values for foams F1–F4, the localized motion of soft segments, however, is not influenced by the increase in the hard segment content thereby suggesting no major changes in microphase separation. In addition, the $T_{1\rho}(^1\mathrm{H})$ and $T_{1\rho}(^{13}\mathrm{C})$ values do indicate that the phase separation of the hard and soft segments is similar for all foams F1–F4. This conclusion is consistent with those of the earlier and previously reported SAXS and thermal analysis results for foams F1–F4.[1,2] The decrease in the $T_{1\rho}(^1\mathrm{H})$ values for the hard segments with increasing LiCl content are a result of the morphological changes that occur upon its addition to the formulation of foams 44-4 and 44-5. Also, the decrease in the soft segment $T_{1\rho}(^1\mathrm{H})$ and $T_{1\rho}(^{13}\mathrm{C})$ values indicate that the motion of the soft segments is more restricted by the hard segments in foams 44-4 and 44-5 in comparison to

44-0. As discussed above, this is believed to be due to more phase mixing in the LiCl foams, which corresponds with our earlier reported results obtained by SAXS, DSC, and TEM.[4]

REFERENCES

1. R. B. Turner, H. L. Spell, and G. L. Wilkes, *SPI 28th Ann. Tech. Market. Conf.*, 244 (1984).
2. J. P. Armistead, G. L. Wilkes, and R. B. Turner, *J. Appl. Polym. Sci.*, **35**, 601 (1988).
3. J. C. Moreland, G. L. Wilkes, and R. B. Turner, *J. Appl. Polym. Sci.*, to appear.
4. J. C. Moreland, G. L. Wilkes, R. B. Turner, E. Rightor, *J. Appl. Polym. Sci.*, to appear.
5. E. O. Stejskal, J. Schaefer, M. D. Sefcik, and R. A. McKay, *Macromolecules*, **14**, 275 (1981).
6. J. Schaefer, M. D. Sefcik, E. O. Stejskal, and R. A. McKay, *Macromolecules*, **14**, 188 (1981).
7. L. W. Jelinski, J. J. Dumais, F. C. Schilling, and F. A. Bovey, *ACS Symposium Series*, No. 191, 345 (1982).
8. J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).
9. L. W. Jelinski, *Macromolecules*, **14**, 1341 (1981).
10. L. W. Jelinski, J. J. Dumais, and A. K. Engel, *Macromolecules*, **16**, 403 (1983).
11. V. J. McBriety and D. C. Douglass, *Macromol. Rev.* **16**, 295 (1981).
12. L. C. Dickenson, P. Morganelli, C. W. Chu, A. Petrovic, and W. J. Macknight, *Macromolecules*, **21**, 338 (1988).