

Investigation of PMMA/Polyoxide Blends Containing Graft-Copolymer Compatibilizers by Using NMR, SEM, and Thermal Analysis

MARCIA C. V. AMORIM,^{1,2,*} CLARA M. F. OLIVEIRA,¹ and MARIA INÊS B. TAVARES¹

¹Instituto de Macromoléculas Professora Eloisa Mano/Universidade Federal do Rio de Janeiro, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ, Brazil, CP 68525, Cep 21945-970; ²Instituto de Química, Universidade do Estado do Rio de Janeiro, R. São Francisco Xavier 527, Maracanã, Rio de Janeiro, RJ, Brazil, Cep 20559-900

SYNOPSIS

The effects of blend compatibility caused by compatibilizing agents were studied by microscopy, thermal analysis, and nuclear magnetic resonance (NMR) spectroscopy (carbon-13 NMR spectra and proton spin-lattice relaxation time) of homopolymers and polymer blends. In this study the results obtained by all measurements are discussed in terms of molecular mobility and compatibility, as a consequence of changes in the microdomains.

© 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends have been the subject of important research works. This interest can be justified because of the shorter time and lower cost of product development than those of a new polymer and also because of the possibility of tailoring the product.¹ In those blends most polymer pairs are not miscible and the compatibility can be enhanced by the adding of a third component (e.g., block or graft copolymer) to the blend. The compatibilizer can reduce the interfacial energy between the matrix and the dispersed phase.²

The blends of poly(methyl methacrylate) (PMMA) and polyoxides have been studied in the past. Because the attention has been centered on systems where one of the components is crystallizable, most of the work presented results of PMMA and poly(ethylene oxide) (PEO) blends where PEO molecular weight is high and the two polymers were assumed to be miscible in the molten state.³ For blends containing PEO of lower molecular weight, PMMA and PEO were found to be compatible up to 20% of PEO.⁴ Blends of PMMA and

poly(propylene oxide) (PPO) were also studied and were considered to be compatible up to 25% of PPO.⁴

By adding an interfacially active graft or block copolymer whose graft or block chains are miscible or partially miscible in one of the components, it can produce a stabilization in the interface of the blend by acting as a compatibilizer.⁵ This can be observed by scanning electron microscopy (SEM) because of the reduction of the domain size and better dispersion in the matrix.^{6,7}

Thermal analysis can also show enhancement of blend compatibility by presenting shifts in glass transition temperature (T_g) at each phase of the blend.^{7,8}

The compatibility of the blends can also be studied by high-resolution solid state nuclear magnetic resonance (NMR).

High-resolution solid state NMR⁹⁻¹³ has been widely used to characterize the heterogeneity of solid polymers. Since the proton spin-lattice relaxation time in a rotating frame ($T_1^H\rho$) can provide detailed information on the molecular and segmental motion,¹¹⁻¹³ the $T_1^H\rho$ and the cross-relaxation time values can be used to characterize the motion of polymers and their blends, as these parameters are functions of nature and the environment of the carbon nuclei. In this study, the carbon-13 NMR spectra were obtained by using cross-polarization/magic-

* To whom correspondence should be addressed.

Table I Graft Copolymers Used as Compatibilizing Agents

Copolymer	Composition (% graft chain)		Molecular Weight	
	PEO	PPO	M_n ^a	M_w ^b
PMMA- <i>g</i> -PEO ^c	18.2	—	27.250	—
PMMA- <i>g</i> -PPO ^d	—	16	20.650	—
PMMA- <i>g</i> -(PEO; PPO) ^e	13.2	13.6	30.240	62.320

^a By GPC.^b By VPO.^c cop PEO.^d cop PPO.^e cop Bigraft.

angle spinning (CP/MAS); the proton relaxation times of homopolymers and polymer blends, with and without copolymer added as a compatibilizer, were also measured.

From this point of view, this work reports the effects caused by the addition of grafted copolymers to blends of PMMA/PEO and PMMA/PPO. These copolymers, which were synthesized by radical copolymerization with a macromonomer technique, are: PMMA-*g*-PEO, PMMA-*g*-PPO, and a bigraft copolymer, PMMA-*g*-(PEO; PPO).^{14,15}

The effects of blend compatibility caused by compatibilizer agents were studied by microscopy, thermal analysis, carbon-13 NMR spectra, and the proton spin-lattice relaxation time of homopolymers and polymer blends.

EXPERIMENTAL

Materials

The homopolymers used in this study were: commercial PEO ($M_n = 1080$); PPO ($M_n = 1000$) (Grupo Ultra, SP, Brazil) and atactic PMMA ($M_n = 110,000$) which was synthesized by radical polymerization in solution.

The graft copolymers used as compatibilizing agents, which were synthesized as described in previous papers,^{14,15} are presented in Table I.

Preparation of the Blends

Blends were prepared in the melt state at 115°C with a Rheomix Plasticorder for 10 min. The mix-

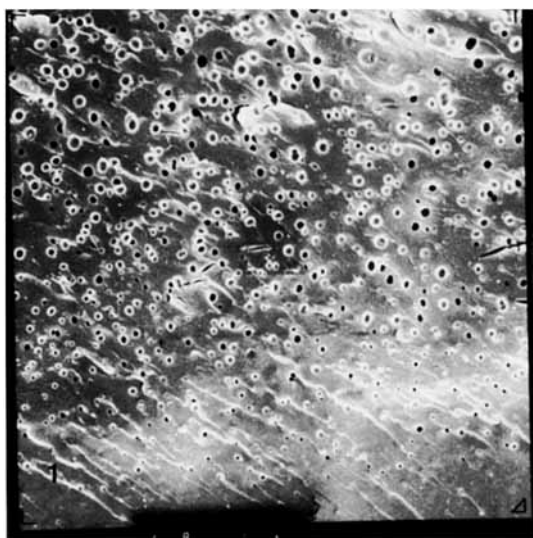


Figure 1 PMMA/PPO (80/20) after extraction with methanol ($\times 1000$).



Figure 2 PMMA after treatment with methanol ($\times 1000$).

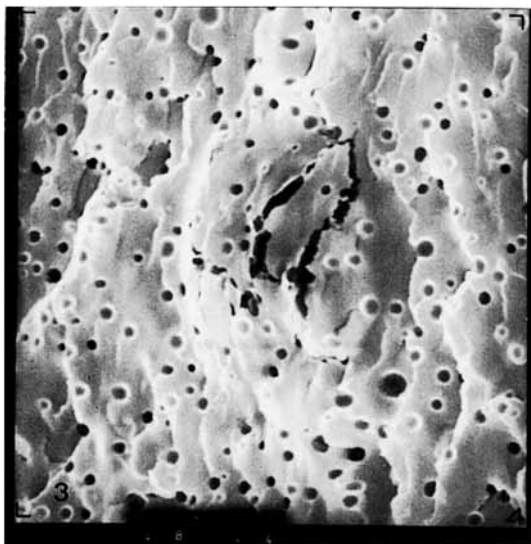


Figure 3 PMMA/PPO (70/30) ($\times 1000$).

tures were then compression-molded under 5000 lbf at 140°C for 5 min and cooled under pressure. All temperatures were chosen based on homopolymer T_g s and thermogravimetric analysis results to provide a homogeneous blend and avoid degradation. Samples with 20% and 30% of polyoxide (PEO or PPO), represented as PMMA/PEO (80/20), PMMA/PEO (70/30); PMMA/PPO (80/20), and PMMA/PPO (70/30), were prepared and the grafted copolymers were added (5%) into blends with 30% of polyoxides (as a rule, the weight percentage of the added copolymer—5%—was defined with respect to the total weight of the blend). The copoly-

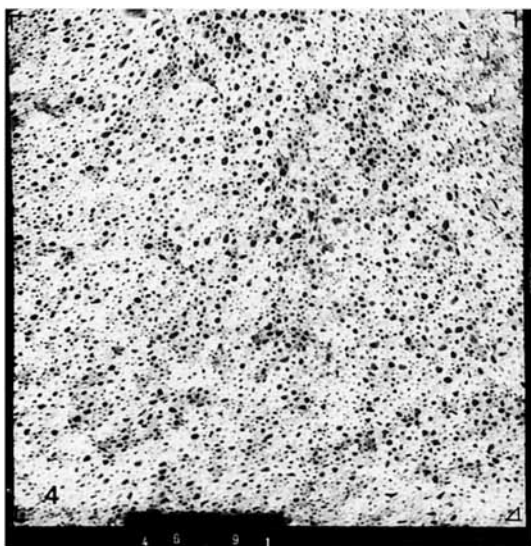


Figure 4 PMMA/PPO (70/30) with PMMA-g-PPO as a compatibilizing agent ($\times 1000$).

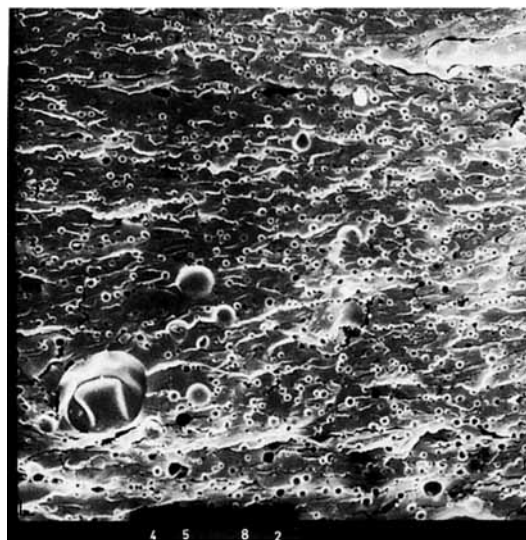


Figure 5 PMMA/PPO 70/30 with PMMA-g-(PEO; PEO) ($\times 1000$).

mer PMMA-g-PEO was added to PMMA/PEO (70/30) blend, the copolymer PMMA-g-PPO to PMMA/PPO (70/30), and PMMA-g-(PEO; PPO) was added to both blends.

Morphology

To study the morphology of the blends, the samples obtained by compression were fractured and etched with methanol for 4 h to extract the polyoxide phase (PEO or PPO) and dried for 6 h. The extraction of the total polyoxide phases is proved by the methanol er transform infrared spectroscopy spectrum. Bands can be observed related to polyoxides. Fractured surfaces were sputtered with gold be-

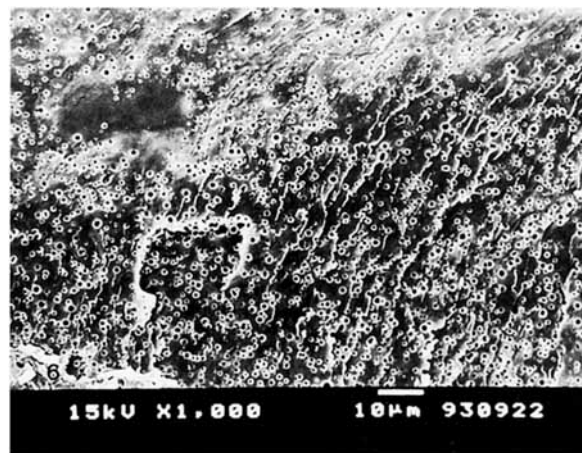


Figure 6 PMMA/PEO (70/30) with PMMA-g-PEO.



Figure 7 PMMA/PEO (70/30) without copolymer ($\times 1000$).

fore viewing under SEM (Jeol JMS U3 or Jeol JSM 5300) at 15 kv electron accelerating voltage.

Thermal Analysis

A Perkin Elmer DSC-7 differential scanning calorimeter (DSC) was used to determine T_g for all the samples after having been molded by compression. They were heated at $10^\circ\text{C}/\text{min}$. under a stream of N_2 .

NMR Measurements

Solid-state carbon-13 CP/MAS NMR techniques were performed on a Varian VXR 300 spectrometer at room temperature. The hydrogen resonance frequency was 299.9 MHz and the carbon-13 resonance frequency was 75.4 MHz. The Hartman-Hahn CP matching and dipolar decoupling filed was ~ 40 KHz, while a $5 \mu\text{s}$ 90-degree pulse for the carbon-13 nucleus was used. The contact time varied from 200 to 8000 μs and the MAS rate was 5 KHz. The T_1^H were obtained from the carbon-13 CP/MAS intensity with increasing contact time.^{16,17} Carbon-13 spectra are correlated with the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm).

RESULTS AND DISCUSSION

Morphology

SEM micrographs of PMMA/PPO (80/20) (Fig. 1) show that the PPO phase is presented as spherical



Figure 8 PMMA/PEO (80/20) ($\times 1000$).

domains, well dispersed in the PMMA matrix. The PPO phase was extracted by methanol, which is a good solvent for PPO and does not attack the PMMA matrix, as seen in Figure 2. This figure presents a SEM micrograph of PMMA after it was treated with methanol, and no effect of the solvent was observed.

As the content of PPO increases, its domain size becomes bigger and not so well dispersed in the matrix, as seen in Figure 3. After the addition of graft copolymer PMMA-*g*-PPO to the blend, the decrease of PPO particle size and the increase of the degree of dispersion can be observed (Fig. 4). The same

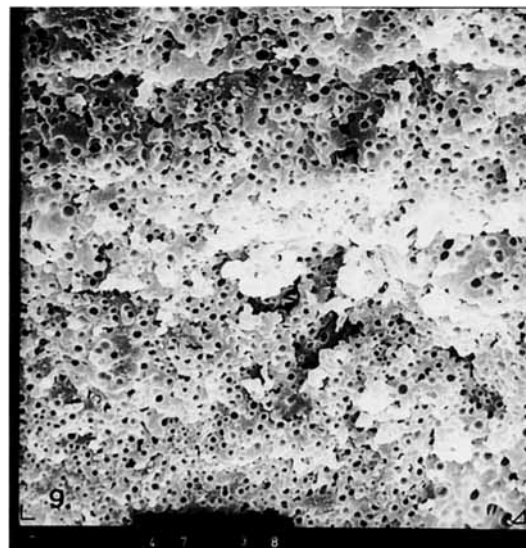


Figure 9 PMMA/PEO (70/30) with PMMA-*g*-(PPO); O ($\times 1000$).

Table II T_g of Polymer Blends

Polymer Blends	Blend Composition			T_g^a (°C)
	PEO	PPO	PMMA (% int)	
PMMA/PEO (80/20)	20	—	80	63
PMMA/PEO (70/30)	30	—	70	88
PMMA/PEO (70/30) cop Bi ^b	30	—	70	79
PMMA/PEO (70/30) cop PEO	30	—	70	75
PMMA/PPO (80/20)	—	20	80	65
PMMA/PPO (70/30)	—	30	70	73
PMMA/PPO (70/30) cop Bi	—	30	70	67
PMMA/PPO (70/30) cop PPO	—	30	70	65

^a T_g measurements were carried out only for high temperature range.

^b cop Bi = PMMA-*g*-(PEO; PPO).

effect can be observed in the blend with 5% of bigraft copolymer PMMA-*g*-(PPO; PEO) added (Fig. 5).

In examining blends of PMMA and PEO, the compatibilizing effect of PMMA-*g*-PEO is also noted. Figure 6 shows a SEM micrograph of PMMA/PEO (70/30) with 5% of graft copolymer where PEO domains (extracted with methanol) are smaller than in the same blend without the compatibilizer (Fig. 7). The domain size and dispersion are equivalent to that of PMMA/PEO (80/20) with a lower content of PEO (Fig. 8). As observed in PMMA/PPO blends, the addition of the bigraft copolymer to PMMA/PEO blends also acts as a compatibilizer, decreasing the interfacial tension and providing a better dispersion of the PEO phase in the PMMA matrix (Fig. 9).

Thermal Analysis

Comparing T_g values (Table II) between PMMA (110°C) and PMMA/polyoxide blends, it can be noticed that there is a decrease in T_g related to the rigid part of the blend PMMA because of the presence of a flexible phase, which is the polyoxide. Comparing the blends with 30% of polyoxide, a decrease in T_g is seen when the graft copolymer is added, probably due to the increase in compatibility between the matrix (PMMA) and the dispersed phase (polyoxides) and confirming the results obtained in microscopy studies. The decrease in T_g related to compatibilizer addition can be observed in both PPO and in PEO blends. Once more, the absence of important differences between PPO and PEO behavior can be related to their low molecular weight.

NMR Analysis

By analysis of an arrayed PMMA, the form of signal distribution from variable contact time, it can be seen that this polymer has a quite homogeneous distribution; a small displacement in the methyl chemical shift was found along the range of spectra, an indication of a heterogeneous sample, which means that PMMA has an atactic configuration. The configurational sequence distribution was determined by triads from solution spectrum in CDCl₃. PMMA shows to be predominantly syndiotactic ($rr = 59.3$, $mr^+ = 36.5$, and $mm = 4.2\%$). The MAS spectrum of PMMA was also recorded and again small displacements were found in the chemical shifts, which corroborated with the existence of more than one domain with different mobilities.

The PEO, when analyzed by variable contact time (VCT), showed just one rigid domain, which was assigned as crystalline domain; only one large resonance line was found at 72.6 ppm. Therefore, the MAS spectrum showed two peaks of resonance, one located at 70.9 ppm (which can be related to the amorphous phase between rigid domains) and another positioned at 61.7 ppm (which belongs to the amorphous region). The comparison between CP/MAS and MAS spectra confirms the existence of at two domains with different mobilities.

PPO was analyzed in solution. It was possible to characterize the presence of more than one configurational sequence. Figure 10 shows the PPO carbon-13 NMR solution spectrum, where the distinct regions are assigned. The peaks exhibit the microstructures (isotactic, syndiotactic, and heterotactic).

Both copolymers (mono and bigraft) exhibit quite homogeneous signal distribution. Therefore, looking

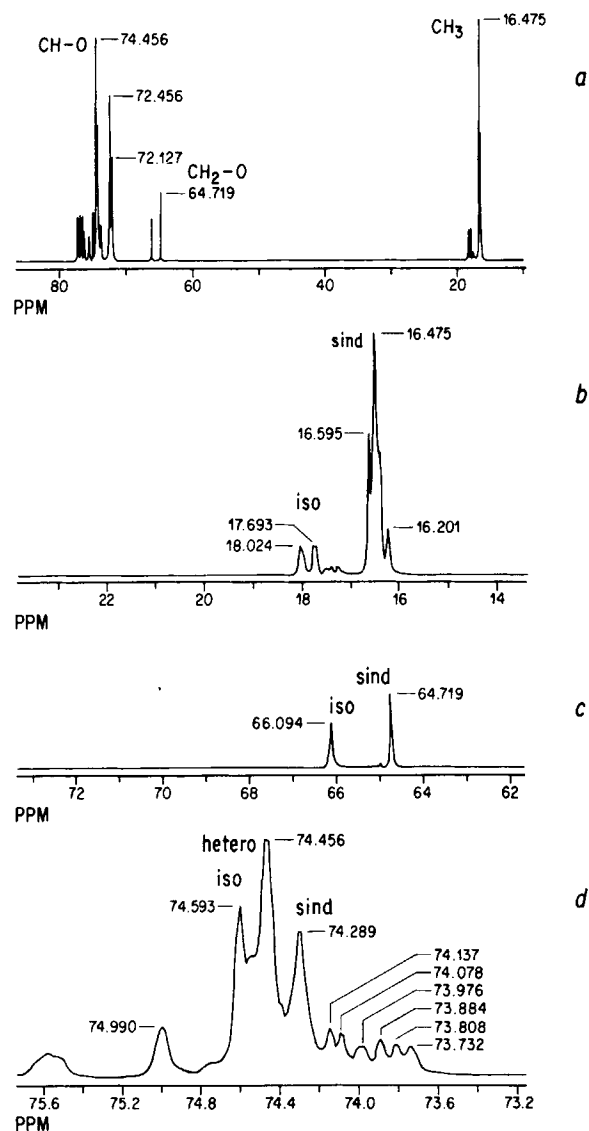


Figure 10 (a) Carbon-13 NMR solution spectrum of PPO; (b) methyl region expansion; (c) methylene oxide region expansion; (d) methyne oxide region expansion.

at the carbon-13 NMR MAS spectra, the same changes in the chemical shifts and peak intensities were observed when compared with CP/MAS spectra. The mobility region is formed by polyoxides and PMMA.

Detailed studies of molecular mobility for PMMA/PEO and PMMA/PPO systems were carried out, carefully analyzing the values of proton $T_{1\rho}$ obtained from the slopes of the peak intensities of the blend spectra plotted versus cross-polarization contact times. Table III illustrates the values for proton spin-lattice relaxation in the rotating frame for three types of carbons of pure PMMA and in

Table III Proton Spin-lattice Relaxation in the Rotating Frame ($T_{1\rho}^{H\rho}$) Measurements for Three Types of Carbons of Pure PMMA and in Blends with PPO, such as Quaternary, Methylene, and Methyl

Sample	$T_{1\rho}^{H\rho}$ (ms)		
	52.5 ^a	45.5 ^a	16.3 ^a
PMMA	4.1	2.6	2.9
Cop Bi	5.1	2.8	4.6
PMMA/PPO 80/20	4.0	2.5	3.3
PMMA/PPO 70/30	4.4	2.8	4.0
PMMA/PPO 70/30 cop PPO	3.8	2.5	3.0
PMMA/PPO 70/30 cop Bi	4.6	2.7	2.5

^a δ ¹³C (ppm).

blends with PPO such as quaternary, methylene, and methyl.

Analyzing the PMMA/PPO 70/30 composition, a small increase in the mobility of methyl resonance of the PMMA can be observed because of the plasticization effect created by adding PPO; the chains seem to be more separated, which can be an indication of phase separation, especially when compared with the 80/20 composition. However, the addition of either copolymer PMMA-*g*-PPO (mono) and bigraft PMMA-*g*-(PPO; PEO) does not make a significant difference in the PMMA mobility. Therefore, this fact may be representative of an interaction that makes the chains more intimately linked by the compatibilization effect.

Table IV illustrates the values for proton spin-lattice relaxation in the rotating frame ($T_{1\rho}^{H\rho}$) for

Table IV Proton Spin-lattice Relaxation in the Rotating Frame ($T_{1\rho}^{H\rho}$) Measurements for Three Types of Carbons of Pure PMMA and in Blends with PEO, such as Quaternary, Methylene, and Methyl

Sample	$T_{1\rho}^{H\rho}$ (ms)		
	52.5 ^a	45.5 ^a	16.3 ^a
PMMA	4.1	2.6	2.9
Cop Bi	5.1	2.8	4.6
Cop PEO	6.8	3.2	5.7
PMMA/PEO 80/20	2.2	4.2	4.7
PMMA/PEO 70/30	3.8	2.5	3.0
PMMA/PEO cop PEO	2.1	3.8	4.7
PMMA/PEO 80/20 cop Bi	1.6	2.6	2.0
PMMA/PEO 70/30 cop Bi	1.6	2.6	—

^a δ ¹³C (ppm).

three types of carbons of pure PMMA and in blends with PEO, such as quaternary, methylene, and methyl.

The values of T_1^H for the blends indicate that the 80/20 PMMA/PEO composition is more compatible than the 70/30.

The influence caused by the addition of mono graft copolymer to the blends is not as expressive as the addition of a bigraft copolymer. When the bigraft copolymer was added to the PMMA/PEO system, it caused a rigidity in the blends, probably due to the induction of the formation of a strong interaction between the two homopolymers; that can be related to a better compatibility of the system. This effect permits us to conclude that the bigraft acts as a better compatibilizer when compared with the monograft copolymer.

CONCLUSIONS

From all of the results of DSC analysis, SEM, and the proton spin-lattice relaxation time in the rotating frame, one can conclude that both graft copolymers (bigraft and monograft) act as compatibilizers in the PMMA/PPO and PMMA/PEO systems.

From the proton spin-lattice relaxation time in the rotating frame, the PMMA/PEO system is more compatible than PMMA/PPO, especially when a copolymer bigraft is added as a compatibilizer agent.

The authors are grateful to PETROBRÁS/CENPES/DIQUIM for the use of the NMR spectrometer; Laboratório de Membranas PAM/COPPE/UFRJ for the use of the scanning electron microscope; and Conselho Nacional de Desenvolvimento e Pesquisa Conselho de Ensino para Graduados e Pesquisa, CEPG/UFRJ for the financial support of this research.

REFERENCES

1. B. Brahimi, A. Ait-kadi, A. Aggi, and R. Fayt, *J. Polym. Sci., Part B, Polym. Phys. Ed.*, **29**, 945 (1991).
2. Jung Whan Kiui and Sung Chue Kim, *Polym. Adv. Technol.*, **2**, 177 (1991).
3. B. J. Kim and R. S. Porter, *J. Polym. Sci., Part B, Polym. Phys. Ed.*, **26**, 2499 (1988).
4. A. S. Liberman, M. Macchi, and A. S. Gomes, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2809 (1984).
5. S. Hosada, H. Kihara, K. Kojima, and Y. Doi, *Polym. J.*, **23**, 277 (1991).
6. R. Fayt and P. H. Tissie, *Polym. Eng. and Sci.*, **29**, 538 (1989).
7. H. C. Kim, K. H. Nam, and W. H. Jo, *Polymer*, **34**, 4043 (1993).
8. T. Duschek and H. Schneider, *Polym. Bull.*, **24**, 317 (1990).
9. J. Schaefer, E. O. Stejskal, and R. Buchdal, *Macromolecules*, **8**, 291 (1975).
10. D. E. Axelson and K. E. Russell, *Polym. Sci.*, **11**, 221 (1985).
11. E. O. Stejskal and J. D. Memory, *High Resolution NMR in the Solid State*, Oxford University Press, New York, 1994.
12. M. I. B. Tavares, E. E. C. Monteiro, A. M. Kenwright, and R. K. Harris, *Polym. Bull.*, **30**, 637 (1993).
13. M. I. B. Tavares, E. E. C. Monteiro, R. K. Harris, and A. M. Kenwright, *Eur. Polym. J.*, **30**, 1089 (1994).
14. C. M. F. Oliveira and A. S. Gomes, *Polym. Bull.*, **22**, 401 (1989).
15. M. C. V. Amorim and C. M. F. Oliveira, *Eur. Polym. J.*, **28**, 449 (1992).
16. N. M. Silva and M. I. B. Tavares, *Polym. Testing*, **14**, 329 (1995).
17. M. I. B. Tavares, W. P. Castro, and D. A. Costa, *J. Polym. Sci.*, **30**, 1085 (1995).

Received June 15, 1995

Accepted January 14, 1996