ELSEVIER

PII: S0032-3861(97)00516-8

Polymer Vol. 39 No. 11, pp. 2143–2147, 1998

0032-3861/98/$19.00+0.00

Investigations of graft copolymer compatibilizers for blends of polyethylene and liquid-crystalline polyester: 2. N.m.r. study

J. Grobelny and D. Sęk*
Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland
(Received 9 August 1996; revised 12 May 1997)

Graft copolymers of functionalized polyethylene having free carboxylic groups (PEox) and liquid-crystalline polyester SBH (derived from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid) prepared under various conditions were investigated by means of high-resolution solid-state ^{13}C nuclear magnetic resonance spectroscopy. Fractionation products of the graft copolymers and a mixture of PEox with SBH were also studied. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: functionalized polyethylene; liquid-crystalline polyester; graft copolymers)

INTRODUCTION

Graft copolymers combining the properties of two different polymers are widely used as new types of material[1]. They can also be used as compatibilizers, i.e. interfacial agents, in the preparation of blends[2–5]. Usually, the blocks of the compatibilizer are identical to the blend components. Their use is mainly in blends of flexible thermoplastics with liquid-crystalline polymers.

Previously, we examined by various methods[6–8] the graft copolymers and mixtures of functionalized polyethylene having lateral carboxylic groups (PEox) with the semi-flexible liquid-crystalline polyester SBH (derived from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid in a mole ratio of 1:1:2), which are expected to serve as compatibilizer in the preparation of blends of polyethylene and SBH. In this work an attempt was made to characterize the structure of these systems by means of high-resolution solid-state ^{13}C nuclear magnetic resonance (^{13}C CP/DD/MAS n.m.r.) spectroscopy.

EXPERIMENTAL

Materials

The following three groups of products were studied:

(1) the mixture (MIX) of PEox with liquid-crystalline polyester SBH;
(2) the copolymer (COP) of PEox with monomers from which the SBH polyester was made; and
(3) the products of catalytic transesterification reactions of PEox and SBH carried out for 15, 60 and 120 min (COP15, COP60 and COP120).In all the cases the weight ratio of PEox to SBH was about 1:1.

Also, the corresponding xylene-insoluble (RX) and toluene-soluble (NC) products of extractions of these polymers were investigated. They were designated respectively as:

(1) RXM and NCM;
(2) RXC and NCC; and
(3) RXC15, NCC15, RXC60, NCC60, RXC120 and NCC120.Details concerning preparation of the samples and the scheme of the extractions are presented elsewhere[6–8].

Measurements

High-resolution solid-state ^{13}C n.m.r. experiments were performed at 20°C on a Varian VXR 300 spectrometer operating at the ^{13}C resonance frequency of 75 MHz. The spectra were acquired by using Hartmann–Hahn spin lock cross-polarization (CP) along with dipolar decoupling (DD) and magic-angle sample spinning (MAS). In the present study the matched spin lock CP transfer employed ^{13}C and ^{1}H magnetic fields of 20 kHz. Proton decoupling was provided at the strength of 55 kHz. The sample spinning at magic angle was carried out at rates between 4 and 5 kHz in a Doty Scientific Co. solids n.m.r. probe. About 200 mg of the samples, as received or cryogenically ground, were compacted into zirconia rotors with Vespel end caps. For all the polymers studied the spectra were acquired with 500–1000 scans and 3 to 15 s delay between pulse sequence repetitions. Spin–lattice relaxation times for protons, T_1^H, were obtained from a $180°-\tau-90°$ pulse sequence followed by simultaneous 200 μs ^{13}C and ^{1}H spin lock and then acquisition of the ^{13}C magnetization with ^{1}H decoupling[9]. Chemical shifts relative to tetramethylsilane (TMS) were determined from the aromatic carbon line (132.1 ppm) of hexamethylbenzene (HMB) used as a standard.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C CP/DD/MAS n.m.r. spectra of SBH and PEox. The spectrum of SBH (*Figure 1a*) exhibits several signals which can be identified, in order of increasing magnetic field, as lines arising from the ester

---

* To whom correspondence should be addressed

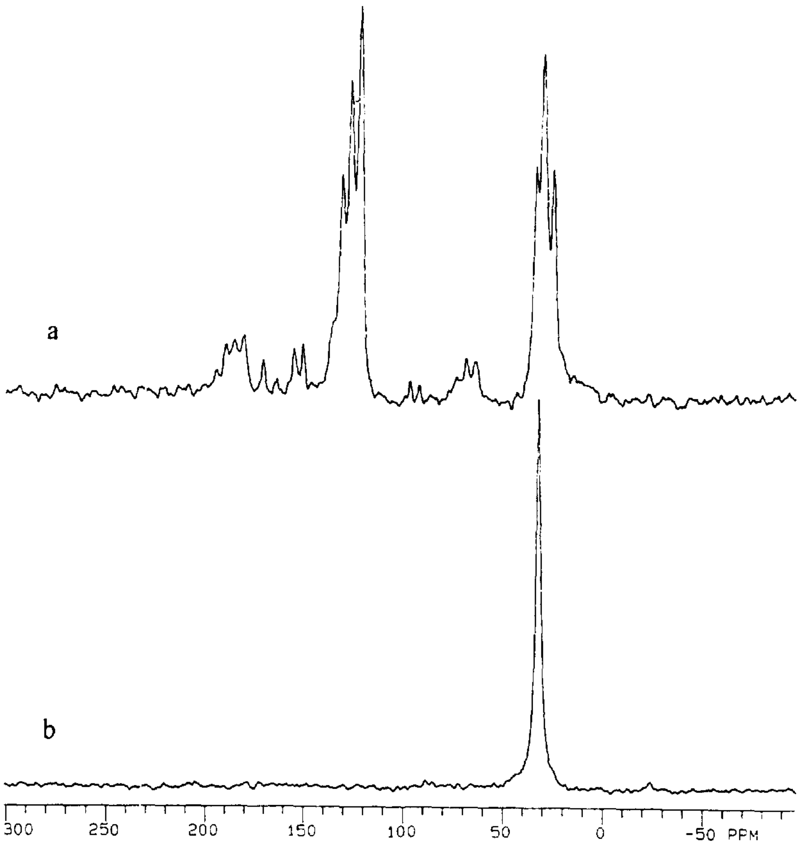

Figure 1 75 MHz ^{13}C CP/DD/MAS n.m.r. spectra of (a) SBH and (b) PEox. The spectra were obtained with 200 μs contact time, 3 s delay between pulse sequence repetitions and 500–1000 scans. The sample spinning at magic angle was carried out at rates between 4 and 5 kHz. Chemical shifts are given relative to TMS

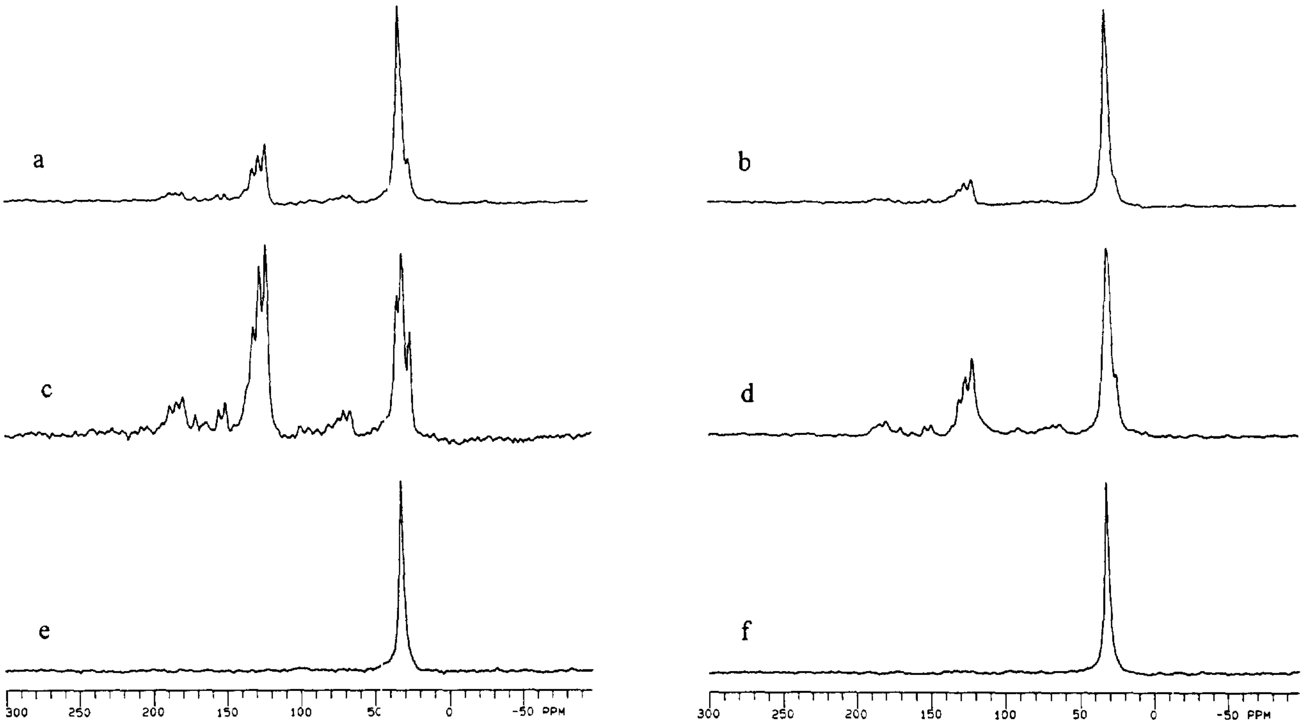

Figure 2 75 MHz ^{13}C CP/DD/MAS n.m.r. spectra of (a) MIX, (b) COP, (c) RXM, (d) RXC, (e) NMC and (f) NCC. The spectra were obtained with 200 μs contact time, 3 s delay between pulse sequence repetitions and 500–1000 scans. The sample spinning at magic angle was carried out at rates between 4 and 5 kHz. Chemical shifts are given relative to TMS

Table 1 Proton spin–lattice relaxation times, T_1^H, of SBH, PEox, MIX and COP

Chemical shift (ppm)	T_1^H (s)			
	SBH	PEox	MIX	COP
131.7	0.73		1.14	0.41
127.4	0.74		1.21	0.56
122.8	0.73		1.21	0.51
34.5	0.80			
32.5	—	4.60	1.98	0.61
31.0	0.74			
25.8	0.80		1.45	0.52

carbons of two types (aliphatic–aromatic at 171 ppm and aromatic–aromatic at 163 ppm), aromatic carbons bonded to oxygens (155.3 and 150.4 ppm) and the carbons connecting the rings in biphenyldiol (136.4 ppm). The lines at 131.7, 127.4 and 122.8 ppm can be ascribed to the protonated aromatic carbons of biphenyldiol and *p*-hydroxybenzoic acid units. Aliphatic carbons of SBH give rise to the resonances observed at 34.5, 31.0 and 25.8 ppm. The remaining lines are the spinning sidebands of aromatic and ester carbon resonances.

The methylene carbon resonance of PEox appears at 32.5 ppm (*Figure 1b*). Lines from CH_3 end groups and COOH lateral groups are not seen in the spectrum.

The spectra of SBH/PEox mixture (MIX) and SBH/PEox copolymer (COP) samples (*Figures 2a* and *2b*) exhibit the lines from the corresponding components (i.e. SBH and PEox). Also, the spectra of xylene-insoluble and toluene-soluble fractions of MIX (RXM and NCM) and of COP (RXC and NCC) are provided in *Figure 2*. The spectrum of RXM (*Figure 2c*) closely resembles that of SBH, which indicates that no chemical reaction occurred between the components of MIX. On the contrary, a salient feature of the RXC spectrum (*Figure 2d*) is the presence of signals due to both components. A decrease in the line intensity of the PEox component relative to the intensities of the lines in the aromatic carbon region is a result of the removal of unreacted PEox macromolecules from the COP sample. As follows from the spectra presented in *Figures 2e* and *2f*, the NCM and NCC samples contain exclusively the PEox component (no aromatic signals of SBH were found).

The examination of proton relaxation behaviour provides information on the homogeneity or heterogeneity of solids. The $T_{1\rho}^H$ and T_1^H relaxation times are influenced by the efficiency of spin diffusion among protons of the constituent polymers. This efficiency is dependent upon the spatial proximity of chemically different chains. In a compatible binary blend, the protons of the two components are closely coupled and relax with a common rate via the spin diffusion mechanism. In the linear additivity model, the relaxivity of the blend should then lie within the bounds of the relaxation rates of the two components. Proton spin diffusion is effective over 200 Å for T_1^H and 20 Å for $T_{1\rho}^H$. On the contrary, the observation of multicomponent relaxation time shows that the dimensions of the separated domains are larger than these values[10,11].

In order to characterize the heterogeneity of SBH/PEox systems on a scale indicated by T_1^H, the values of spin–lattice relaxation time for protons were measured from individual, highest-intensity carbon lines of the constituent polymers. The T_1^H data for SBH, PEox, MIX and COP are summarized in *Table 1*.

In the case of MIX, the T_1^H assume values intermediate between those of the source polymers (*Table 1*). However, they differ from each other; the average values for SBH and PEox components of MIX being about 1.2 and 2 s, respectively. The inequality of the T_1^H relaxation time values reveals a heterogeneity in MIX with the domain dimensions exceeding several hundred Å. The changes in T_1^H as compared with the values observed in the source polymers may indicate considerable structural variations of the components upon mixing, with possible interactions between the domains. By means of the extraction processes the MIX sample could be separated into two samples: RXM containing pure SBH and NCM consisting of pure PEox. The T_1^H values in these samples were found to be close to those observed in the corresponding components of MIX and quite different from the values characteristic for the source polymers (*Tables 1 and 2*).

In COP the T_1^H relaxation is faster than for either component (*Table 1*). Such a behaviour may arise from any motional and conformational changes imposed by copolymerization as well as from changes in molecular packing and domain dimensions. As in MIX, a difference in T_1^H exists between SBH (0.5 s) and PEox (0.6 s) components of COP. This indicates that, in COP, the spin diffusion among protons of the copolymer constituents over a distance of several hundred Å is also incomplete. The difference is, however, considerably lower (0.1 s for COP *versus* 0.8 s for MIX), which suggests an enhancement in the intimacy of mixing due to chemical modification. Moreover, the significant decrease in the T_1^H values of both components relative to those found in MIX may indicate reduced molecular dimensions of the domains. A further decrease in T_1^H values observed for the xylene-insoluble RXC fraction (*Table 2*) may be due to the removal of pure PEox, which was found to be present in the toluene-soluble NCC sample. For the latter the T_1^H value was considerably lower than that measured for the starting PEox. These observations reveal changes in the PEox morphology.

Table 2 Proton spin–lattice relaxation times, T_1^H, of RXM and NCM obtained after extraction of MIX and of RXC and NCC obtained after extraction of COP

Chemical shift (ppm)	T_1^H (s)					
	MIX	RXM	NCM	COP	RXC	NCC
131.7	1.14	1.06		0.41	0.33	
127.4	1.21	1.12		0.56	0.35	
122.8	1.21	0.99		0.51	0.37	
34.5		1.11				
32.5	1.98	—	1.90	0.61	0.47	1.21
31.0		1.08				
25.8	1.45	1.12		0.52	0.34	

The ^{13}C CP/DD/MAS n.m.r. spectra of the products of catalytic transesterification reactions of PEox and SBH (COP15 and COP60) and the compounds obtained after extraction (RXC15 and RXC60) are presented in *Figure 3*. It follows from the spectra that the RXC15 sample contains no measurable amounts of PEox which means that, according to n.m.r. measurements, the corresponding COP15 consists of an unreacted mixture of SBH and PEox. With increasing reaction time the transesterification occurs, as seen by the presence of the line due to PEox in the spectrum of RXC60, i.e. the xylene-insoluble fraction of COP60.

The values of spin–lattice relaxation times, T_1^H, of these samples are provided in *Table 3*. Although COP15 seems to be an unreacted mixture of SBH and PEox, the T_1^H relaxation times for COP15 are lower than for MIX. It can thus be concluded that the intimacy of mixing in COP15 is better than in MIX. Likewise, the structure of RXC15 differs from that of RXM even though the both samples contain exclusively unreacted SBH. Unexpectedly, in COP60 the average values of T_1^H were found to be similar to those in MIX and quite different from those observed in COP. This is probably due to a relatively low degree of conversion of the reaction between SBH and PEox. With further increase in the reaction time (COP120) the T_1^H tends to approach the value found in COP, which probably results from the enhanced conversion and lower amount of unreacted PEox. The difference between SBH and PEox components is, however, much less in the catalytic condensation products than in MIX (0.1 s for COP60 and COP120 *versus* 0.8 s for MIX) and close to that found for COP. All these observations are presumably accounted for by differences in morphology and/or in chemical structure (the average length of SBH chains grafted onto PEox and the amount of PEox carboxyl groups involved in the reaction with SBH) of the copolymers obtained by various routes.

After extraction, the values for RXC60 and RXC120 decrease as compared with those for COP60 and COP120, respectively, which is most probably related to the reduced amount of unreacted PEox component. As previously mentioned, an analogous tendency was observed in the case of the extraction of COP leading to RXC.

The spectra of the toluene-soluble fractions (NCC15, NCC60 and NCC120) revealed only the presence of PEox component. For these samples the spin-lattice relaxation times, T_1^H, were measured (*Table 3*) and compared with the value previously obtained for the source PEox (4.6 s). A significant decrease in T_1^H was observed for NCC15, NCC60 and NCC120 (1.2–1.3 s) which can be interpreted in terms of some changes in morphology and/or molecular mobility of PEox.

It is worth noting that the proton relaxation behaviours presented in this paper are consistent with the morphological investigations on the studied systems carried out by differential scanning calorimetry and scanning elctron microscopy techniques. The MIX was found to exhibit the

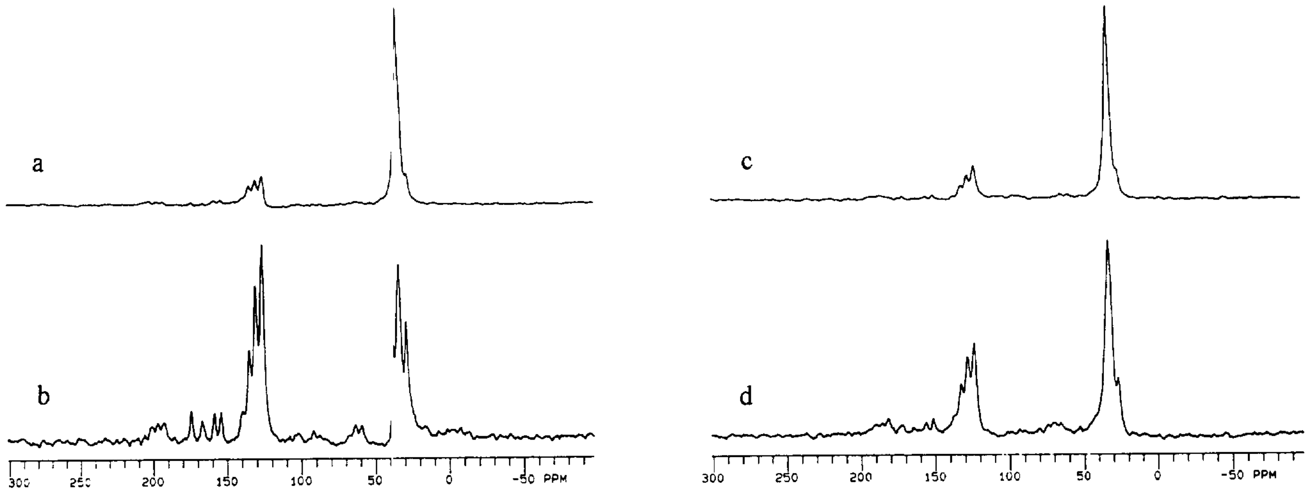

Figure 3 75 MHz ^{13}C CP/DD/MAS n.m.r. spectra of (a) COP15, (b) RXC15, (c) COP60 and (d) RXC60. The spectra were obtained with 200 μs contact time, 3 s delay between pulse sequence repetitions and 500–1000 scans. The sample spinning at magic angle was carried out at rates between 4 and 5 kHz. Chemical shifts are given relative to TMS

Table 3 Proton spin-lattice relaxation times, T_1^H, of the products of catalytic transesterification reactions of PEox and SBH carried out for 15, 60 and 120 min (COP15, COP60, COP120) and of the compounds obtained after their extraction (RXC15, NCC15, RXC60, NCC60, RXC120 and NCC120)

Chemical shift (ppm)	T_1^H (s)								
	COP15	RXC15	NCC15	COP60	RXC60	NCC60	COP120	RXC120	NCC120
131.7	0.95	0.99		1.13	0.96		0.83	0.71	
127.4	1.08	0.93		1.22	0.99		0.96	0.88	
122.8	1.01	0.89		1.21	1.09		0.94	0.79	
34.5		0.92							
32.5	1.15	—	1.15	1.04	0.79	1.22	0.79	0.64	1.27
31.0	0.98	0.87							
25.8		0.87		1.00	1.04		0.84	0.71	

biphasic morphology typical for a blend of immiscible polymers. Also, a two-phase structure was observed in COP. MIX was concluded to be made up of two separated phases poorly dispersed in one another, whereas for COP the phase dispersion, though not uniform, was found to be much finer and the interphase interactions to be much more pronounced[7,8].

ACKNOWLEDGEMENTS

This work was carried out within a Copernicus Program (contract no. CIPA-CT 94-0118) founded by the Commission of the European Communities.

The authors express sincere thanks to Professor P. L. Magagnini of the University of Pisa and Professor L. Minkova of the Institute of Polymers, Bulgarian Academy of Sciences in Sofia, for providing the samples.

REFERENCES

1. La Mantia, F. P., in *Thermotropic Liquid Crystal Polymer Blends*. Technomic Publishing Co. Inc., Lancaster–Basel, 1993.
2. Fayt, R., Jerome, R. and Teyssie, P., *Makromol. Chem.*, 1986, **184**, 837.
3. Noolandi, J. and Hong, K. M., *Macromolecules*, 1984, **17**, 1531.
4. Lai, Y.-C., *J. Appl. Polym. Sci.*, 1994, **54**, 1289.
5. Brown, H. R., Daline, V. R. and Green, P. F., *Nature*, 1989, **341**, 221.
6. Sęk, D. and Kaczmarczyk, B., *Polymer*, 1997, **38**, 2925.
7. Magagnini, P. L., Paci, M., Minkova, L. I., Miteva, Ts., Sęk, D., Grobelny, J. and Kaczmarczyk, B., *J. Appl. Polym. Sci.*, 1996, **60**, 1665.
8. Minkova, L. I., Miteva, Ts., Sęk, D., Kaczmarczyk, B., Magagnini, P. L., Paci, M., La Mantia, F. P. and Scaffaro, R., *J. Appl. Polym. Sci.*, 1996, **62**, 1613.
9. Sullivan, M. J. and Maciel, G. E., *Anal. Chem.*, 1982, **54**, 1615. and references therein.
10. Linder, M., Henrichs, P. M., Hewitt, J. M. and Massa, D. J., *J. Chem. Phys.*, 1985, **82**, 1585.
11. Jong, L., Pearce, E. M., Kwei, T. K. and Dickinson , L. C., *Macromolecules*, 1990, **23**, 5071.