N.m.r. studies on the transesterification of polycarbonate/poly(ethylene terephthalate) blends

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The chemical structures of copolymers formed in the transesterification of polycarbonate/poly(ethylene terephthalate) blends during melt processing were deduced from the ^{1}H n.m.r. spectra of reaction products which were extracted in CH_2Cl_2 solvent (extracted soluble and insoluble products). The changes in the extent of reaction with the reaction conditions (reaction time, temperature and blend composition) were also interpreted by the changes of peak intensity of typical peaks in ^{1}H n.m.r. spectra.

(Keywords: n.m.r. spectra; transesterification; blends)

Introduction

Recently, there has been considerable scientific and industrial interest in the transesterification of polyesters. The bisphenol A polycarbonate (PC)/poly(ethylene terephthalate) (PET) system has attracted commercial interest, since both polymers are widely used as engineering plastics. In particular, PC has high impact strength and its solvent resistance is improved by mixing with PET. Since both PC and PET are polyesters, transesterification can easily occur during melt processing, which has a great effect on the compatibility and mechanical properties of PC/PET blends.

Devaux and co-workers[1–3] studied the possible reactions in PC/PET blends during melt processing. It was considered that the main reaction occurring in molten PC/PET blends was the exchange reaction (transesterification); other subsequent reactions were degradation, pyrolysis and gel formation, probably due to the instability of the ethylene carbonates produced by the exchange reactions. Some copolymers were formed in the reactions of PC/PET blends but their structures were only qualitatively characterized by *FT*i.r. Recently, Runt *et al.*[4] analysed the ^{1}H n.m.r. spectra of reaction products of polyarylate/poly(butylene terephthalate) blends to calculate the average sequence lengths and degrees of randomness of copolymers in the blends. As any changes in chemical shift are most likely due to protons of copolymers in transesterification of the blends, we expect to determine the structures of copolymers in the blends with ^{1}H n.m.r. combined with Soxhlet extraction. In addition, the changes of reaction extent with the reaction conditions (reaction time, temperature and blend composition) were also interpreted by the changes of peak intensity of typical peaks in ^{1}H n.m.r. spectra.

Experimental

Both PC and PET were kindly supplied by Beijing Institute of Chemical Engineering. The viscosity average molecular weight of PC was 3.0×10^4 g mol^{-1} and that of PET was 2.0×10^4 g mol^{-1}. Blends with different compositions were prepared: PC/PET (wt%) 100/0, 80/20, 50/50, 20/80 and 0/100. Blends were first dissolved in mixed solvent (phenol:1,1,2,2-tetrachloroethane in a 60:40 ratio by weight), then precipitated with methanol to obtain the samples. The samples were dried in a vacuum oven at 60°C for 1 day and at room temperature for a few weeks.

Transesterification of PC/PET blends was carried out in an oven under dry nitrogen atmosphere. Blends with different reaction extents were obtained by changing the reaction conditions.

Reaction products were extracted in CH_2Cl_2 solvent. Extraction was carried out until the weight of insoluble products did not change. The extracted soluble products were precipitated with methanol. Then the soluble and insoluble products were dried for ^{1}H n.m.r. analysis. ^{1}H n.m.r. spectra were recorded on a Bruker Unity-200 n.m.r. spectrometer with a field strength of 200 MHz. Samples were dissolved in proton-decoupling solvent (CF_3COOD for the insoluble products and $CDCl_3$ for the soluble products). Tetramethylsilane was used as internal standard.

Results and discussion

^{1}H n.m.r. spectra can be used to obtain more direct evidence for transesterification of PC/PET blends and its progress with the changes of reaction conditions. The n.m.r. spectra of PC and PET are shown in *Figure 1* along with peak assignments.

The extracted insoluble products included unreacted PET and PET blocked into some PC segments[5] for PC/PET (20/80) blends which were heat treated at 280°C

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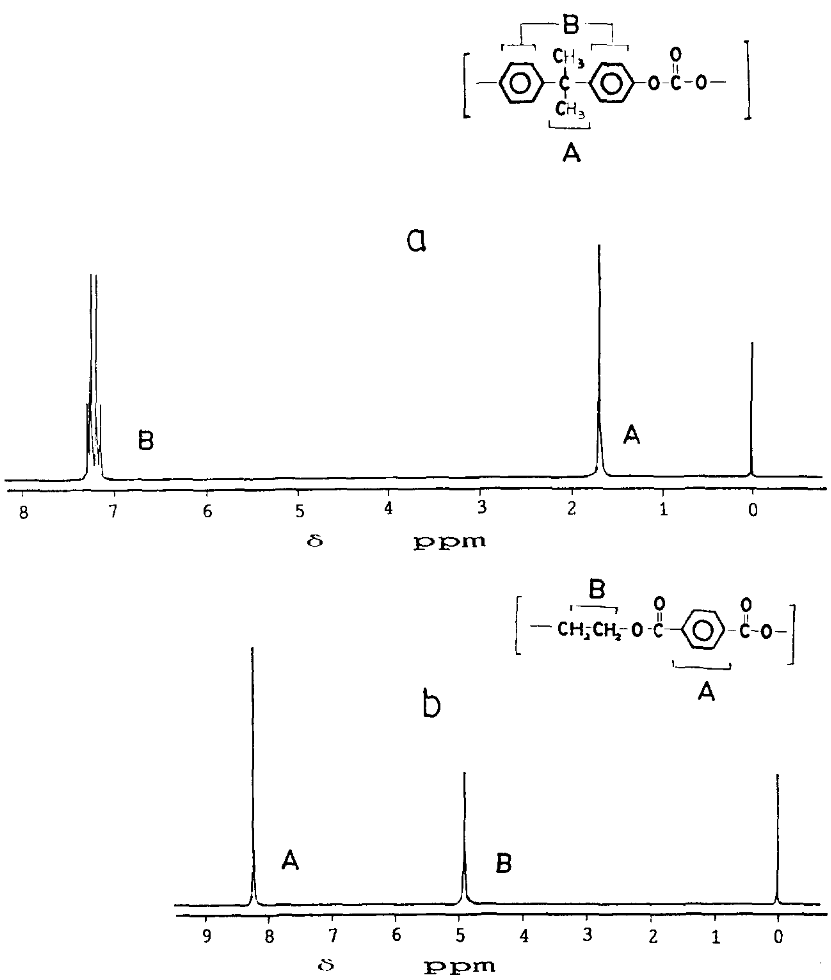

Figure 1 ^{1}H n.m.r. spectra of (a) PC and (b) PET

for 5 min and 20 min; the n.m.r. spectra are shown in *Figures 2a* and *b*, and the possible peak assignments are indicated in *Table 1*. As would be expected, there were not only typical chemical shifts of PET but also chemical shifts of PC segments coexisting in the n.m.r. spectra. In addition, two new peaks, corresponding to 3.68 and 8.38 ppm, were discerned in the spectra. These results can be explained by the formation of copolymers in the transesterification of PC/PET blends, in which the new peaks corresponded to those of copolyesters formed in the reactions. The structure of copolyester in *Figures 2a* and *b* can be deduced from the above results as follows:

$$\text{PC—OCOOCH}_2\text{CH}_2\text{—PET}$$

In addition, the peak intensity of new peaks gradually increased with increasing reaction time. As the peak intensity is closely associated with the number of protons, the results indicated that the amount of copolyesters increased with the increase of reaction time for PC/PET blends (20/80). So the extent of reaction in the blends also increased, which is in agreement with the results of *FT*i.r. analysis[5].

The extracted soluble products included unreacted PC and PC blocked into some PET segments[5] for PC/PET (80/20 and 50/50) blends which were heat treated at 280°C for 20 min; the n.m.r. spectra are shown in *Figures 2c* and *d*, and the possible peak assignments are indicated in *Table 2*.

As well as the ^{1}H n.m.r. results of the insoluble products shown in *Figures 2a* and *b*, there were not only typical chemical shifts of PC but also chemical shifts of PET, which confirmed that some PET segments were blocked in the PC phase. In addition, some new peaks (8.26, 6.80, 6.65, 4.25 and 3.65 ppm) were discerned in the n.m.r. spectra, which were attributed to the formation of copolymers. The structure of this copolymer can also be determined as follows:

$$\text{PC—OOC—PET}$$

The changes of peak intensity of new peaks were also used to characterize the changes of reaction extent for blends with different blend compositions. From the data in *Table 2*, it can be concluded that PC/PET (50/50) blends had a higher reaction extent than PC/PET (80/20) blends with the same reaction conditions.

Combining the n.m.r. spectra of extracted soluble and insoluble products in CH_2Cl_2 solvent, the possible reaction mechanism in PC/PET blends during melt processing can be deduced as follows:

$$\begin{array}{ccc} \text{PC—OCOO—PC} & & \text{PC—OCOOCH}_2\text{CH}_2\text{—PET} \\ + & \rightarrow & + \\ \text{PET—COOCH}_2\text{CH}_2\text{—PET} & & \text{PC—OOC—PET} \end{array}$$

Conclusions

The chemical structure of block copolymers formed in the transesterification of PC/PET blends was deduced

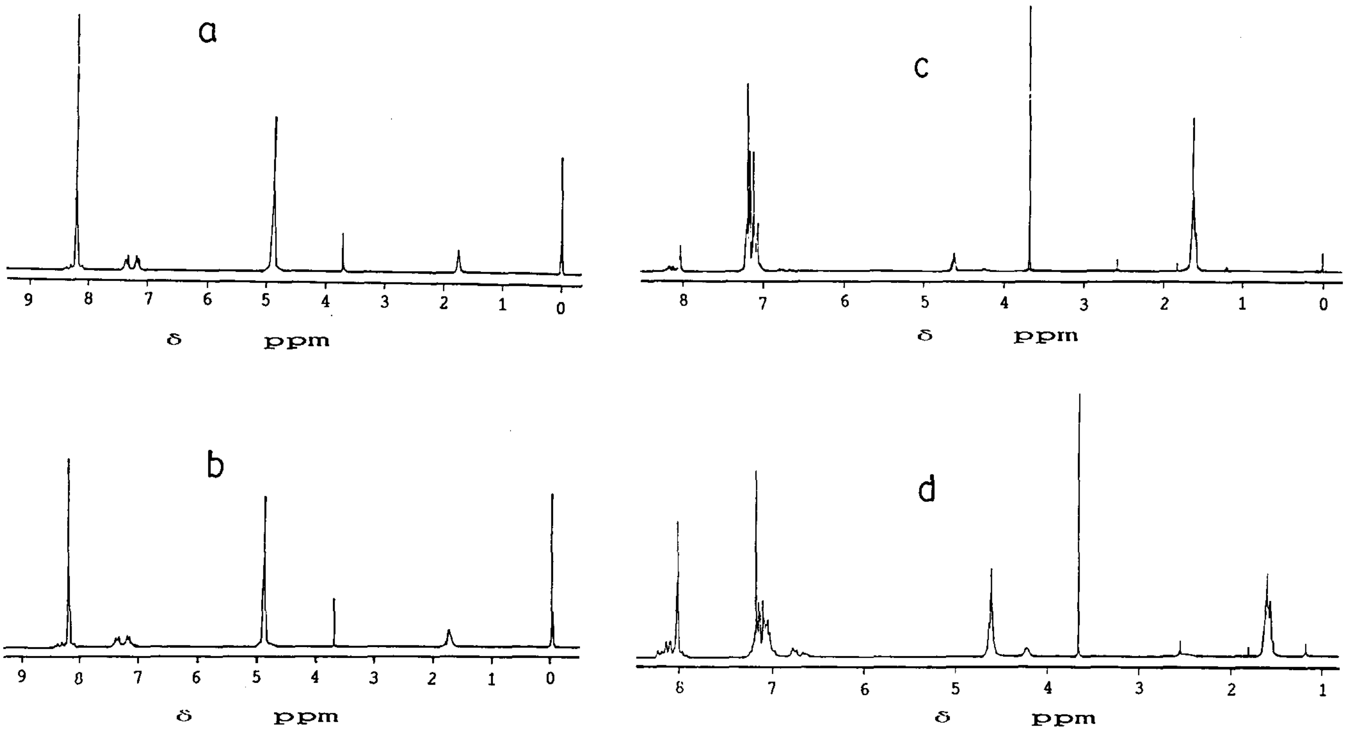

Figure 2 ^1H n.m.r. spectra of extracted insoluble products in PC/PET (20/80) blends heat treated at 280°C for (a) 5 min and (b) 20 min, and of extracted soluble products in blends heat treated at 280°C for 20 min, (c) PC/PET = 80/20 and (d) PC/PET = 50/50

Table 1 Effect of the transesterification times on the peak position (δ) and intensity (*I*) of the typical peaks in ^1H n.m.r. spectra of the extracted insoluble products in PC/PET (20/80) blends which were heat treated at 280°C for 5 min (a) and 20 min (b)

	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)
PET	8.16	49.62	4.90	49.62								
					7.34	5.83						
a	8.22	38.93	4.89	38.62	7.18	5.32	8.36	1.04	3.70	3.08	1.75	8.18
					7.31	6.50						
b	8.22	36.54	4.89	36.45	7.21	6.86	8.38	1.32	3.68	3.84	1.75	9.82

Table 2 Effect of the blend compositions on the peak position (δ) and intensity (*I*) of the typical peaks in ^1H n.m.r. spectra of the extracted soluble products in the PC/PET (80/20) (c) and PC/PET (50/50) (d) blends, which were heat treated at 280°C for 20 min

	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)	δ (ppm)	*I* (%)
PC	7.23	29.12	7.18	29.12	1.66	41.76						
					1.61				4.25	1.14	6.65	2.52
c	7.19	22.42	7.11	22.42	1.58	31.93	8.20	6.71	4.63	5.46	3.66	6.16
					1.60				4.20	2.75	6.65	4.04
d	7.19	14.36	7.11	14.36	1.57	23.3	8.25	16.7	4.61	14.2	3.66	6.89

from the ^1H n.m.r. spectra of both the extracted soluble and insoluble reaction products in CH_2Cl_2 solvent and the possible reaction mechanisms of transesterification in the PC/PET blends were proposed. N.m.r. results also showed that the reaction extent of PC/PET blends was closely associated with reaction conditions (reaction time, temperature and blend composition). The extent of reaction increased with increasing reaction time and PC/PET (50/50) blends had the highest extent of reaction with the same reaction conditions. These results were in agreement with *FT*i.r. results, which indicated that ^1H n.m.r. is also an effective tool for characterizing the transesterification of polymer blends.

Acknowledgement

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