# Phase Behavior and Transreaction Studies of Model Polyester/Bisphenol-A Polycarbonate Blends. 3. Midchain and Alcoholysis Reactions

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ABSTRACT: Detailed proton NMR examination of transreacting poly(2-ethyl-2-methylpropylene terephthalate) (PEMPT)/Bisphenol-A polycarbonate (PC) 50/50 (w/w) blends enables the simultaneous monitoring of both alcoholysis and midchain transreactions. In the absence of midchain reaction, alcoholysis via the hydroxypropylene end group of PEMPT and the carbonate group of PC enhances miscibility over a range of molecular weights. At the transition point from two phase to single phase, 5.7 mol % of the PEMPT repeat units are connected to PC via alcoholysis. In a PEMPT/PC blend of high molecular weight undergoing simultaneous alcoholysis and midchain reaction, the extent of reaction required to shift the phase behavior from two phase to one phase is 4%. This corresponds to 2.8% alcoholysis and 1.2% midchain transreaction. These levels of reaction required for phase transition are in theoretical agreement with simple models of the reacting blend.

## Introduction

Having identified the phase behavior of nontransreacted PEMPT/PC blends,[1] the quantitative relationship between transreaction and phase behavior will now be examined. Similar to discussions on poly(butylene terephthalate) (PBT)/PC and poly(ethylene terephthalate) (PET)/PC blends, there are four possible interchange reactions to be concerned with:[2,3] (1) direct midchain transreaction between a carbonyl of PEMPT and a carbonate of PC; (2) alcoholysis of PC by a hydroxyl end group of PEMPT; (3) acidolysis of PC by an acid end group of PEMPT; (4) alcoholysis of PEMPT by a hydroxyl end group of PC.

As discussed previously, many studies have identified transreactions either directly (NMR, IR) or indirectly from phase behavior (DSC, DMTA, and microscopy).[4] In any indirect study of exchange reaction, the separate role of midchain and end-group transreactions is unidentifiable. In studies that have employed direct measures of interchange reaction, specifically $^1H$ and $^{13}C$ NMR, none have assigned any observed resonances to a specific end group in the blend under observation.[5−15] Thus, most of these studies ignore the role of separate reactions. In actuality, the low concentration of end groups combined with the insolubility of the polyesters studied makes end-group identification difficult.

In their kinetic studies of model compounds transreacting with PBT and PC and in their kinetic study of a transreacting PBT/PC blend, Devaux et al. concluded that alcoholysis did not play a major role in the interchange process and that direct midchain reaction is the most likely mechanism of randomization during transreaction of a PBT/PC blend.[2,6] These conclusions could also be drawn from several other facts. With alcoholysis of PBT by PC phenol end groups not observed and with carbonate acid end groups (resulting from acidolysis) known to be unstable (decomposing to carbon dioxide and a phenol end group), once all of the PBT hydroxyl and acid end groups have transreacted no other end-group reactions can occur.[16,17] With the percentage of end groups being relatively low, less than 2−3%, extensive randomization of the blend components could only be achieved through midchain reactions. It should be mentioned that in Devaux's studies, end-group reaction was determined indirectly by molecular weight changes monitored by viscosity measurements. No direct spectroscopic identification was made.

From this information, it appears that midchain reaction plays the dominant role in the extensive transreaction of polyester/PC blends, the role of alcoholysis being inconsequential. This may lead one to ignore alcoholysis of PC by PEMPT hydroxyl end groups, concluding that this reaction is insignificant. However, the present goal is to examine the quantitative effect transreaction has on blend phase behavior. In this case, where small amounts of block copolymers may lead to varying degrees of compatibilization of the blend, end-group reactions may indeed become important.

In the present study, acidolysis of PC by PEMPT acid end groups is deemed to be insignificant for two reasons. First, in the preceding paper of this series, it is demonstrated that end-group reactions up to 16% have only minor effects on phase behavior.[1] In the present case, the carboxylic acid ends are present in extremely small quantities (<2% of the total end-group content at $M_n$s less than 20 000); thus, their effect on blend phase behavior is expected to be negligible. Second, if acidolysis does occur, the resulting carbonate acid end group is known to decompose into species incapable of interchange reaction. Thus, acidolysis cannot lead to extensive randomization of the blend components. Additionally, alcoholysis of PEMPT by PC hydroxyl end groups is also insignificant. Studies on model compounds have shown that this reaction does not occur, and evidence is presented to support this statement for the PEMPT/PC blend.[2] With the proton NMR resonances of the aliphatic-hydroxyl end group of PEMPT identified, the PEMPT/PC blend system offers the unique opportunity to spectroscopically monitor the hydroxyl end groups and, hence, alcoholysis transreactions independent of direct midchain reaction.[4] These two reactions and their subsequent effect on blend phase behavior are the focal point of this paper.

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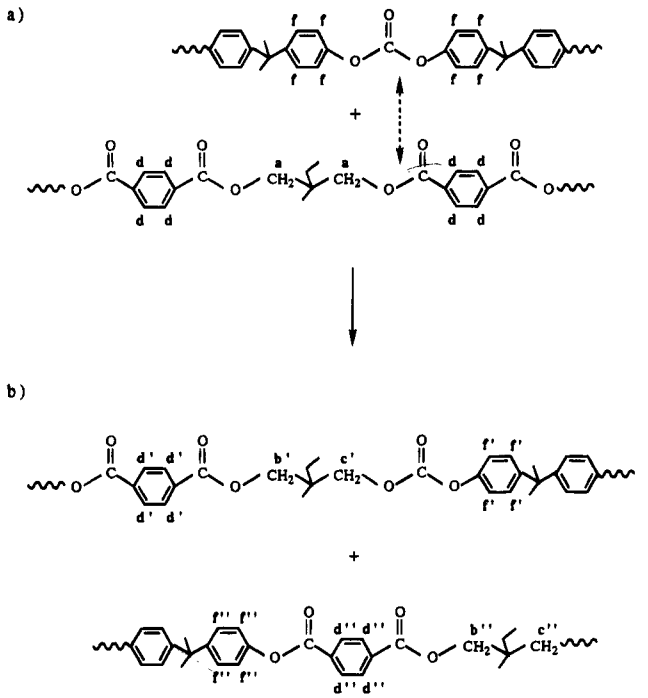

**Figure 1.** Midchain transreaction with proton designations for NMR: (a) reactants; (b) products.

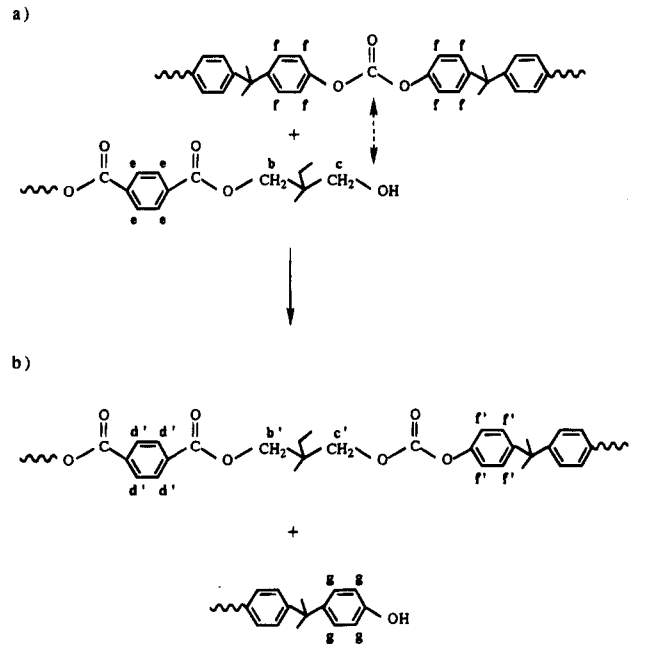

**Figure 2.** Alcoholysis transreaction with proton designations for NMR: (a) reactants; (b) products.

**NMR Protocol.** The proton NMR resonances corresponding to the expected structures after alcoholysis and direct midchain transreaction must be identified and assigned. Previous studies on transreacting polyester and polyester/PC blends have used predominantly diad and to a lesser extent triad analyses to correlate the observed spectra to the structures expected after interchange reaction.[3,5,12,14,15,18] The midchain and end-group structure of PEMPT are shown in Figures 1a and 2a, respectively. The repeat unit of PC is also shown. Proton NMR of PEMPT reveals that the protons of the terephthalate ring adjacent to the aliphatic-hydroxyl end-group, **e** (Figure 2a), are not magnetically equivalent to those of a dual aliphatic–aromatic substituted ring, **d** (Figure 1a).[4] Thus, triad analysis is required

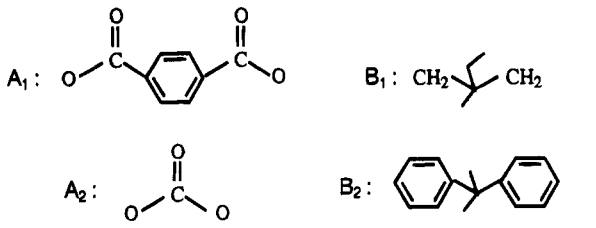

**Figure 3.** Coding for PEMPT and PC sequences.

**Table 1. Pentads Formed after Exchange Reaction between PEMPT and PC (Pentads Centered on the Terephthalate Ring of PEMPT)**

| pentad | no. of transreactions |
|---|---|
| $A_1B_1A_1B_1A_1$ | 0 |
| $A_1B_1A_1B_1A_2$ | 1 |
| $A_1B_1A_1B_2A_2$ | 1 |
| $A_1B_1A_1B_2A_1$ | 2 |
| $A_2B_1A_1B_2A_2$ | 2 |
| $A_2B_1A_1B_2A_1$ | 3 |
| $A_1B_2A_1B_2A_2$ | 3 |
| $A_2B_1A_1B_1A_2$ | 2 |
| $A_2B_2A_1B_2A_2$ | 2 |
| $A_1B_2A_1B_2A_1$ | 4 |

to completely assign the end-group structure of PEMPT. In a blend, interchange reaction may occur on both sides of the terephthalate group; thus, pentad analysis is required for complete structure identification. With the designations shown in Figure 3, the polymer repeat units can be represented as follows:

$$\text{PEMPT} \quad -(A_1B_1)-$$

$$\text{PC} \quad -(A_2B_2)-$$

The expected pentads in a transreacting PEMPT/PC blend can be represented using similar notation. Centering the pentad on a terephthalate ring of PEMPT ($A_1$), 16 different combinations are noted. However, of these, 6 pairs are degenerate. Thus, there are 10 chemically nonequivalent pentads. Table 1 lists these pentads along with the corresponding number of transreactions required to form the sequence.

Due to instrument resolution limitations, assigning all the possible resonances associated with these 10 structures is impossible. To circumvent this problem, relatively low levels of transreaction will be examined. If this restraint is applied, only the statistically most probable pentads will be observed, i.e., the pentads formed from the minimum number of interchange reactions. The statistically most probable pentads are pentads 2 and 3 (Table 1). Combining this with the fact that they represent a degenerate pair, the resonances of these pentads should be the most dominant in the NMR spectra of blends with low levels of transreaction. The two sequences are rewritten as a quartad and a triad, which both focus on the connecting point between the two blocks.

$$A_1B_1\mathbf{A_1B_1A_2} \equiv \mathbf{A_1B_1A_2}B_2$$

$$A_1\mathbf{B_1A_1B_2}A_2 \equiv \mathbf{B_1A_1B_2}$$

These two structures correspond to the block sequences after a single midchain reaction between a carbonyl of PEMPT and a carbonate group of PC. Midchain transreaction and the resulting quartad and triad with alphabetically coded hydrogens are shown in Figure 1a (reactants) and Figure 1b (products). Similarly, Figure

**Table 2. Molecular Weight and End-Group Analysis of PEMPT**

| pentad | $X_n$[a] | mol % of acid end groups |
|---|---|---|
| PEMPT 1-OH | 16.5 | 0.19 |
| PEMPT 2-OH | 24.6 | 0.43 |
| PEMPT 3-OH | 38.3 | 0.53 |
| PEMPT 4-OH | 46.4 | 1.00 |
| PEMPT 5-OH | 73.4 | 1.05 |
| PEMPT 6-OH | 151 | 5.91 |
| PEMPT 7-OH | 71.0 | 2.15 |

[a] From fluoride end-group analysis.

2a and Figure 2b display the alcoholysis interchange reaction and the resulting sequences. It should be noted that midchain and alcoholysis transreaction lead to the identical quartad, reducing the number of resonances to be assigned. NMR analysis of these new structures will focus on identification and assignment of the terephthalate and backbone methylene protons of PEMPT and the aromatic protons of PC.

## Experimental Section

**Polymers and Blends.** The synthesis and characterization of the polyesters used in this study have been reported.[4] The number-average degree of polymerization ($X_n$) and the percentage of acid end groups relative to the total end-group concentration are recited in Table 2. The two Bisphenol-A polycarbonates used in this study were provided by the General Electric Co. They contain no additives. They are designated as PC1 ($X_n$ = 45) and PC2 ($X_n$ = 85). The equipment and conditions used to obtain these results have been reported.[1]

Alcoholysis and its effects on phase behavior were examined using the PEMPT B-OH series of polyesters blended with PC1 and PC2. Specific details of the preparation have been presented.[1] The 50/50 (w/w) blends were prepared by solution casting from chloroform with dioctadecyl phosphite (DNOP) added as a transreaction inhibitor. DNOP is known to inhibit interchange reaction in PBT/PC and PET/PC blends and is used for this purpose.[8,17] In PEMPT/PC blends, DNOP is an effective inhibitor of midchain transreactions; however, at the annealing temperatures and times used in this study, it is not able to completely inhibit alcoholysis.[1] Thus, alcoholysis can be obtained in the absence of midchain reaction. To completely eliminate alcoholysis, an identical series of polyesters were prepared with benzoate end groups.[4] These polyesters are designated as PEMPT BNZ.

Blends for simultaneous midchain/alcoholysis transreaction studies were prepared by a codissolution/precipitation procedure. PEMPT 7-OH (0.35 g) and PC2 (0.35 g) were added to a vial followed by 17 mL of chloroform. After complete dissolution and thorough mixing, the solution was added dropwise to 170 mL of methanol under vigorous mixing. The solution was filtered and the recovered blend was washed with two 25 mL aliquots of fresh methanol. The blend was dried under vacuum at 76 °C for several days and subsequently stored in a vacuum desiccator.

**Analysis.** Thermal analysis for alcoholysis studies (PEMPT B-OH/PC series of blends) was conducted in a Perkin-Elmer DSC-7 with an Intercooler II and nitrogen as the purge gas. Indium and recrystallized dimethyl isophthalate were used as calibration standards. All scans were conducted at 20 °C/min with baseline subtraction. Sample size was ~6 mg. The annealing and scanning programs are outlined below.

| annealing | scanning |
|---|---|
| load at 20 °C | load at 20 °C |
| heat at 100 °C/min to 280 °C | 1st scan, 20 °C/min to 200 °C |
| hold 0.2 min | cool at 50 °C/min to 20 °C |
| cool at 100 °C/min to 200 °C | hold 2 min |
| annealing time: 60 min at 200 °C | 2nd scan, 20 °C/min to 200 °C |
| cool at 50 °C/min to 20 °C | cool at 50 °C/min to 20 °C |

This annealing program was used to ensure that blends were at or near equilibrium.[1] The short annealing period at 280 °C was used to melt the PC crystals that had formed during the casting procedure.

Thermal analysis of the PEMPT 7-OH/PC2 blends was conducted in a Perkin-Elmer DSC-4 with a System 4 thermal analysis microprocessor controller and a thermal analysis data station. A dry ice/ethanol slurry was used for subambient cooling. Indium was the calibration standard, and baseline subtraction was used during the runs. Sample size was 6–8 mg. The annealing and scanning temperature ramps used are shown below. Note that no crystallization of the PC component occurred during the precipitation procedure used to recover the blend; thus, heating to 280 °C was not required.

| annealing | scanning |
|---|---|
| load at 40 °C | load at 40 °C, quench to 20 °C |
| heat at 100 °C/min to 200 °C | 1st scan, 20 °C/min to 200 °C |
| annealing time at 200 °C: variable | quench to 40 °C |
| cool at 50 °C/min to 20 °C | |

Proton NMR was conducted on a Varian 300-XL spectrometer (300 MHz). The samples from DSC analysis were dissolved in deuterated chloroform (1% w/v) with TMS used as an internal reference. The acquisition time was 3.725 s with a delay time between pulses of 7.0 s. Sixty-four scans per sample were recorded. $^1H-^1H$ correlation spectroscopy (COSY) was also conducted on the Varian 300-XL spectrometer. The spectral width was usually narrowed to the frequency region of interest. Specific scanning conditions are detailed during the discussion of the individual spectra.

GPC was conducted using a Waters Model 590 pump combined with a Waters WISP Auto Injector Model 710B. The detector was a Perkin-Elmer Model LC90 variable-wavelength UV detector operated at 254 nm. Three Waters Ultrastyragel columns of $10^5$, $10^4$, and $10^3$ Å were employed. A Nelson Analytical data collection system with series 2600 software was used for data collection/analysis. Chloroform at 1 mL/min was used as the solvent. Narrow molecular weight distribution polystyrene (PS) standards were used for calibration. At the wavelength used for detection, the absorption coefficient for the polyester was considerably greater than that of PC. Hence, GPC analysis on the blend selectively detects the polyester to a large extent.

## Results

**Identification and Assignment of Proton NMR Resonances.** The proton resonances corresponding to PEMPT's midchain and end-group structures (Figures 1a and 2a) have been identified and assigned as follows: **a**, 4.290 ppm (s); **b**, 4.231 ppm (s); **c**, 3.423 ppm (m); **d**, 8.081 ppm (s); **e**, 8.065 ppm (s).[4] The proton resonances of PC will now be briefly discussed. The proton spectrum of PC is straightforward with five main resonances. A singlet at 1.678 ppm is associated with the methyl groups and a pair of doublets with resonances at 7.149, 7.179, 7.238, and 7.268 ppm correspond to the aromatic ring protons (protons **f** in Figures 1a and 2a). Finer splitting of this original pair of doublets is observed. Overall, 11 resonances are detected and an additional resonance is most likely hidden by the chloroform peak at 7.261 ppm.

Aromatic rings with different electron-withdrawing groups in the para position fall into a spin system known as AA'BB'.[19,20] These spin systems may exhibit up to 24 lines in their spectra; however, resolution limitations often prevent observation of all resonances. The importance of this spin system lies in the fact that upon direct midchain reaction, the $B_1A_1B_2$ triad (Figure 1b, protons **d''**) represents this spin system; thus, it can be used as an indication for midchain transreaction. The

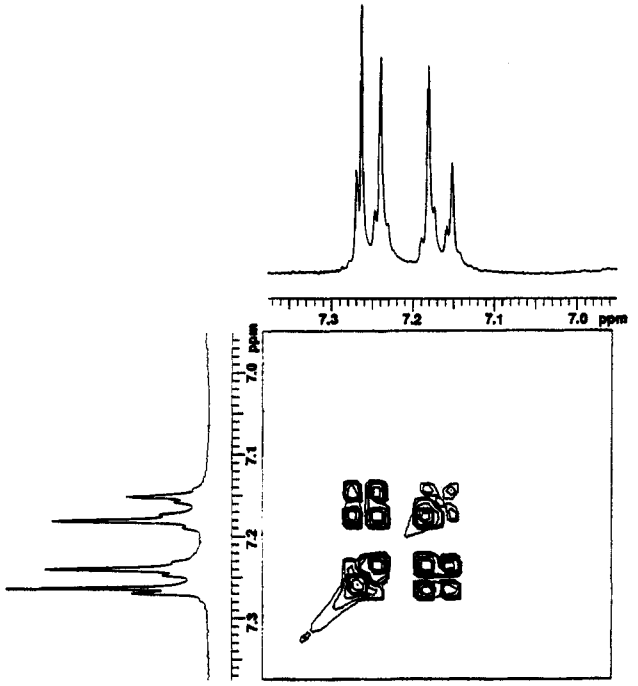


**Figure 4.** 300 MHz $^1$H NMR COSY spectrum of PC2. The aromatic region of the spectrum is displayed.

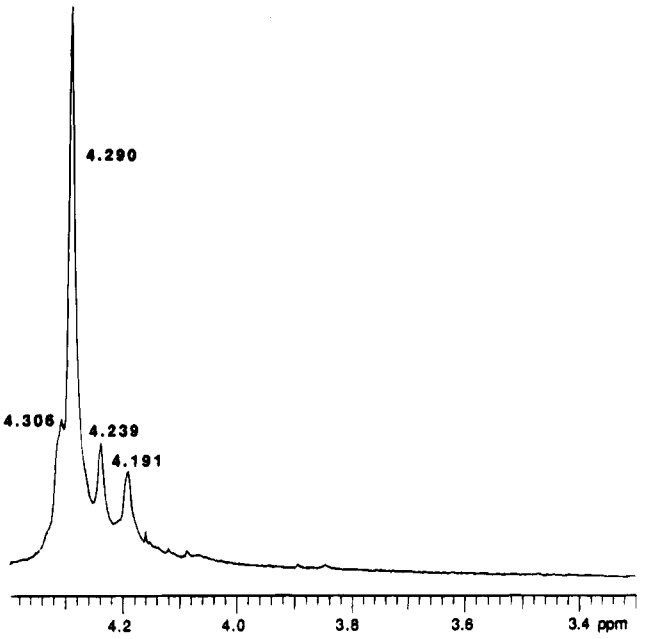


**Figure 5.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed 128 min at 240 °C. The methylene backbone region of the spectrum is displayed.

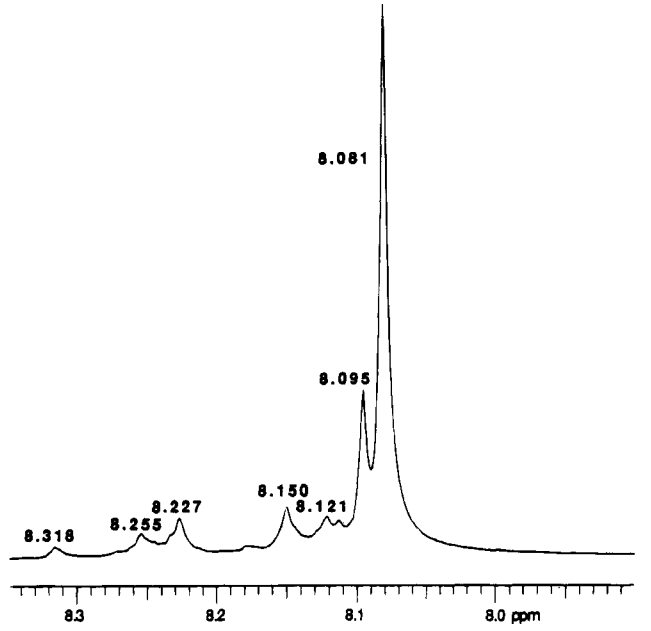


**Figure 6.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed 128 min at 240 °C. The terephthalate region of the spectrum is displayed.

Bisphenol-A sequence of PC will be used as a model for the $^1$H−$^1$H COSY pattern for the AA′BB′ spin system. Figure 4 shows the 300 MHz COSY spectrum of the aromatic region of PC. The pulse width was 9.3 $\mu$s and the spectral width was 6.950−7.376 ppm, with 64 intervals and 16 scans per interval being run. The resulting spectrum, which corresponds to proton correlations in the aromatic ring, exhibits a distinct four-lobe pattern. This pattern will be used as confirmation of midchain transreaction between PEMPT and PC.

Previous $^1$H NMR studies have identified new resonances in both the aromatic (terephthalate group) and aliphatic (methylene group) regions of the spectra during transreaction in polyester and polyester/PC blends.[5,6,12,13,15] It is anticipated that the PEMPT/PC system will exhibit analogous changes in these regions as well as the frequency region associated with PC aromatic rings. Spectroscopic examination will focus on these three portions of the spectrum, ignoring the aliphatic region corresponding to the side chain substitution in PEMPT and the methyl protons of PC. This does not imply that shifts in these aliphatic regions are not observed, but the close proximity of the peaks, combined with splitting, leads to a less certain identification and assignment.

To identify resonances associated with interchange reaction, a PEMPT 7-OH/PC2 blend is allowed to react for 128 min at 240 °C. Proton NMR of the annealed sample displays numerous additional resonances associated with structure changes caused by transreaction. Expansions of the spectrum corresponding to the backbone methylene, terephthalate, and PC aromatic proton regions are shown in Figures 5, 6, and 7, respectively. The chemical shifts of the most prominent new resonances are labeled in each diagram. $^1$H−$^1$H COSY experiments are also run on the annealed sample.

Figure 8 shows the 300 MHz COSY spectrum of the terephthalate region. The spectral width is narrowed to 7.902−8.423 ppm with 64 intervals. Thirty-two scans per interval are run with a pulse width of 9.3 $\mu$s. Examining Figure 8, off-diagonals indicate that both protons resonating at 8.121 and 8.150 ppm are coupled with the protons at 8.227 and 8.255 ppm. The coupling pattern is similar to that observed for the PC model AA′BB′ spin system and indicates that this pair of protons belong to a para-substituted aromatic ring with different electron-withdrawing groups. Similarly, a COSY experiment is conducted encompassing the aromatic region of PC. The spectral window is 7.381−6.948 ppm, which is again divided into 64 intervals. Thirty-two scans are recorded per interval with a 9.3 $\mu$s pulse width. This spectrum is shown in Figure 9. One new AA′BB′ coupling pattern is clearly present, corresponding to coupling of protons resonating at 7.035 and 7.064 ppm with two protons at 7.198 and 7.230 ppm. These last two resonances were not detected in the 1-D $^1$H NMR, being overlapped by the original pair of doublets

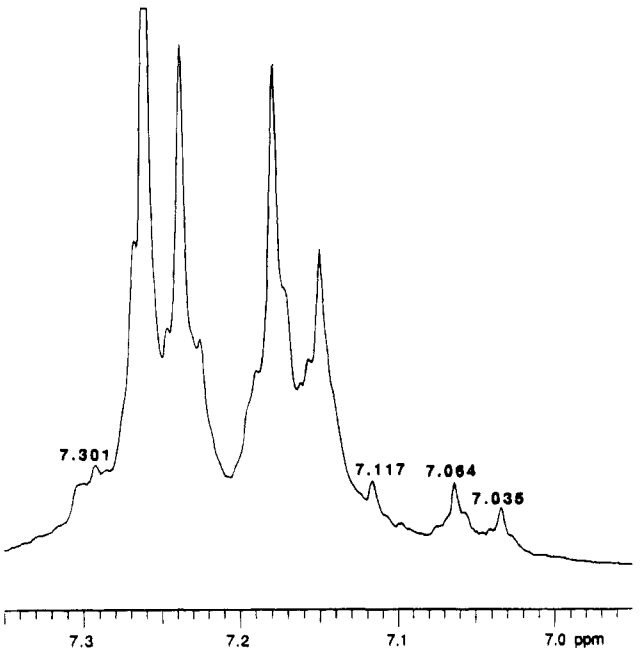


**Figure 7.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed 128 min at 240 °C. The PC aromatic region of the spectrum is displayed.

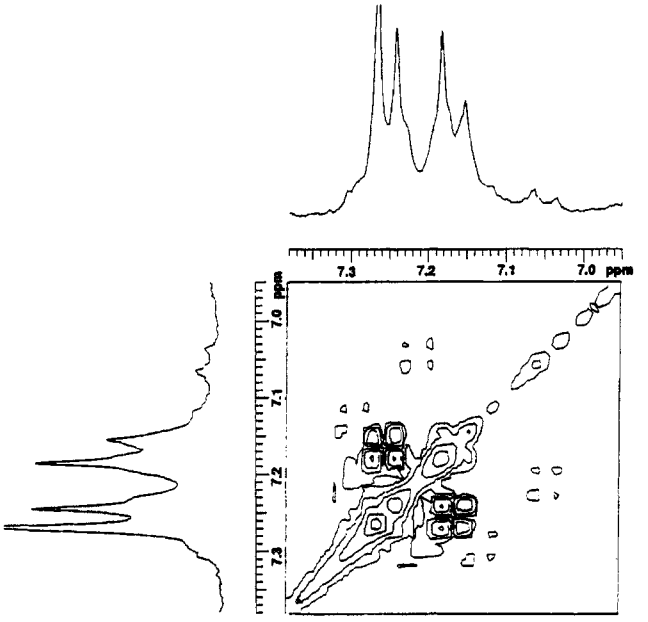


**Figure 9.** 300 MHz $^1$H–$^1$H NMR COSY spectrum of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed 128 min at 240 °C. The PC aromatic region of the spectrum is displayed.

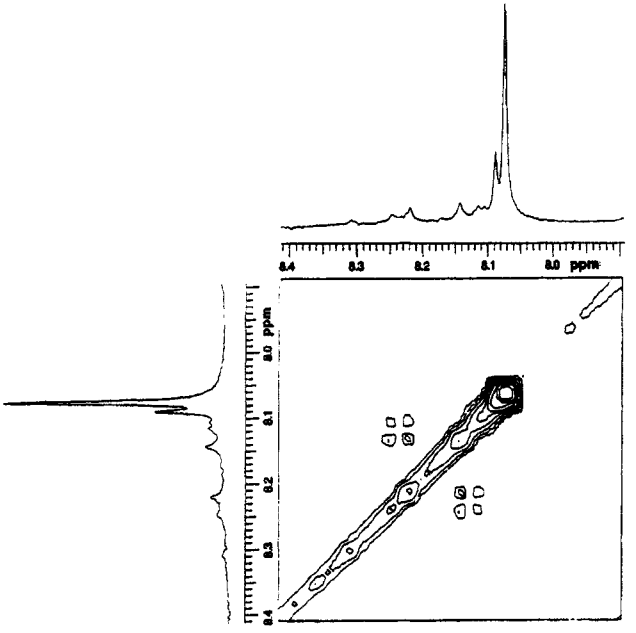


**Figure 8.** 300 MHz $^1$H–$^1$H NMR COSY spectrum of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed 128 min at 240 °C. The terephthalate region of the spectrum is displayed.

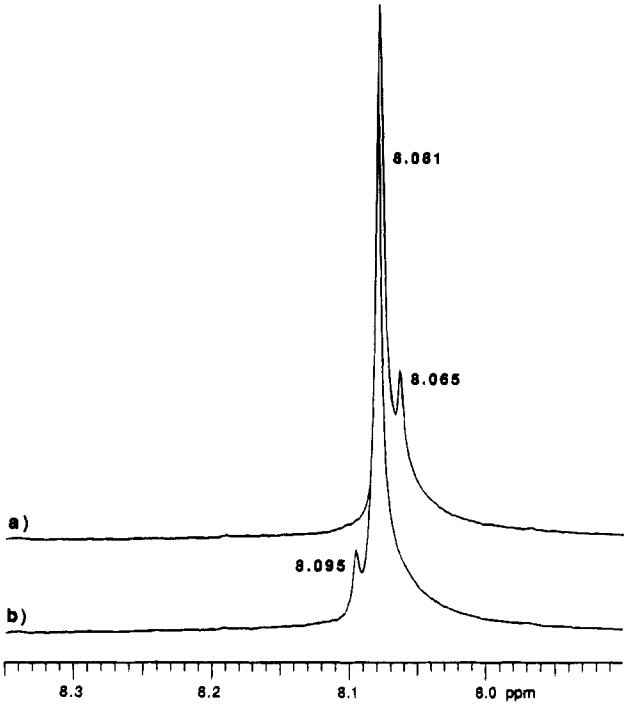


**Figure 10.** 300 MHz $^1$H NMR of a DNOP-stabilized PEMPT 1B-OH/PC1 50/50 blend: (a) as cast; (b) after DSC annealing/scanning. The terephthalate region of the spectrum is displayed.

of the PC aromatic rings. Additionally, another AA'BB' coupling pattern is observed. This off-diagonal pattern slightly overlaps the coupling pattern of the original aromatic protons. Coupling between both resonances at 7.117 and 7.145 ppm with the 7.274 and 7.301 ppm resonances is observed. Again, two additional resonances have been determined from the COSY experiment, 7.145 and 7.274 ppm. These coupling patterns are once again similar to the PC model pattern and indicate that different electron-withdrawing groups are now present in the para position of the PC aromatic ring.

Figures 10a and 10b show the proton NMR spectra displaying the terephthalate region of a PEMPT 1B-OH/PC1 blend (DNOP stabilized) before and after DSC annealing/scanning, respectively. The resonance associated with the terminal terephthalate group, protons **e** (Figure 2b), is observed at 8.065 ppm prior to DSC. After DSC, this resonance is gone and a new resonance at 8.095 ppm (s) appears. Additionally, the resonances associated with the backbone methylene groups adjacent to the hydroxyl terminal group, **b** and **c** (Figure 2b), have been replaced by two new resonances, 4.239 (s) and 4.191 ppm (s). New resonances were also observed in the spectrum corresponding to the aromatic region of PC: 7.101, 7.064, and 7.035 ppm. These results imply that the hydroxyl end groups of PEMPT reacted via alcoholysis with the carbonate group of PC

during the thermal analysis program used for phase identification.

With the most prominent new frequencies in the transreacted blends identified, it is now necessary to assign these frequencies to the structures of Figures 1b and 2b. Beginning with the quartad sequence (identical in Figures 1b and 2b), the resonances at 4.239 and 4.191 ppm are assigned to protons **b′** and **c′**, respectively. The upfield shift from the main methylene backbone resonance is expected upon replacement of the aromatic ester by the less deshielding aromatic carbonate group. The nonsymmetric substitution of the propylene group should also lead to two resonances, as is observed. These assignments are confirmed by the spectroscopic results of the PEMPT 1B-OH/PC1 blend after alcoholysis. Upon alcoholysis, which leads to this same quartet sequence, the identical two resonances are present. Similar upfield shifts have been noted in a model study of oligomers synthesized from phthalic anhydride and 1,2-propanediol.[21] In this study, the methylene backbone resonances depended on triad sequence (midchain vs end group).[21]

Continuing on to the aromatic resonances of PC, replacement of the aromatic portion of Bisphenol-A by the less deshielding propylene group is expected to produce an upfield shift on the remaining adjacent aromatic ring of the quartad, protons **f′**. The four resonances shifted upfield from the original resonances and confirmed by the COSY experiment to have the coupling of an AA′BB′ spin system—7.035, 7.064, 7.198, and 7.230 ppm—are assigned to protons **f′**. Two of these resonances were observed in the proton NMR of PEMPT 1B-OH/PC1 after alcoholysis, confirming these assignments.

Perhaps the most interesting assignment of this quartad sequence is protons **d′** assigned to the resonance at 8.095 ppm. This peak is inconsistent with the diad analysis commonly used for peak assignments in these systems.[5,7] NMR studies of the PEMPT 1B-OH/PC1 blend confirm that the resonance at 8.095 ppm is indeed associated with protons **d′**. After complete alcoholysis, the resonance at 8.065 ppm is replaced by the 8.095 ppm peak.

The assignment of the proton resonances associated with the triad of Figure 1b will now be discussed. Beginning with the terephthalate region of the spectrum, the four new resonances confirmed to be an AA′BB′ spin system—8.150, 8.121, 8.227, and 8.255 ppm—are assigned to protons **d″**. This splitting pattern has been noted in a transreacting PBT/PAr blend.[13] Next, the remaining observed AA′BB′ spin system in the PC aromatic region—resonances 7.117, 7.145, 7.274, and 7.301 ppm—is assigned to the protons **f″**. The final assignment is the resonance at 4.306 ppm to protons **b″**. This assignment is somewhat tentative and represents another instance in this reacted blend where diads do not sufficiently describe all the observed resonances. Table 3 summarizes all of the $^1$H NMR assignments.

Several observed resonances have not been assigned. They include peaks at 8.318, 8.179, and 8.113 ppm. A resonance at 8.28 ppm has been associated with a symmetrically substituted terephthalate ring in a transreacted PBT/PC blend.[5] In the PEMPT/PC blend, the corresponding terephthalate protons of an $A_2B_2A_1B_2A_2$ sequence are assigned to the 8.318 ppm resonance. One possible assignment of the 8.113 ppm resonance is to the terephthalate protons with the symmetrical substitution $A_2B_1A_1B_1A_2$. The shift is ca. twice that observed

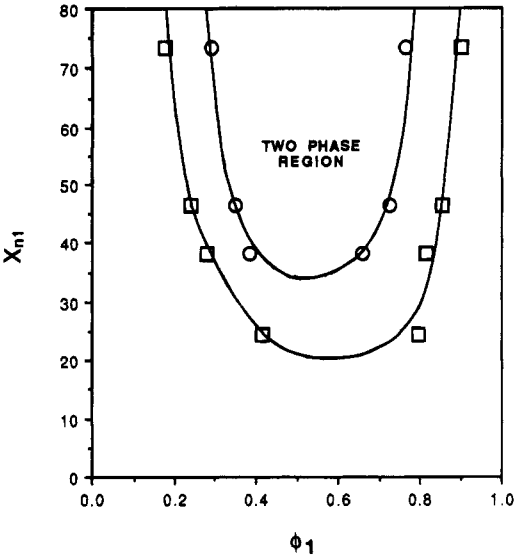


**Figure 11.** Miscibility diagram of DNOP-stabilized PEMPT B-OH/PC1 (○) and PEMPT-BNZ/PC1 (□) 50/50 blends. $X_{n1}$ is the number-average degree of polymerization of PEMPT and $\phi_1$ is the volume fraction of PEMPT.

**Table 3. $^1$H NMR Resonance Assignments of PEMPT and PC after Transreaction**

| backbone methylene | proton assign (ppm) | aromatic Bisphenol-A | proton assign (ppm) | aromatic terephthalate | proton assign (ppm) |
|---|---|---|---|---|---|
| **b′** | 4.239 | **f′** | 7.035 | **d′** | 8.095 |
| **c′** | 4.191 | **f′** | 7.064 | | |
| | | **f′** | 7.198 | | |
| | | **f′** | 7.230 | | |
| **b″** | 4.306 | **f″** | 7.117 | **d″** | 8.150 |
| | | **f″** | 7.145 | **d″** | 8.121 |
| | | **f″** | 7.274 | **d″** | 8.227 |
| | | **f″** | 7.301 | **d″** | 8.255 |

for the formation of an $A_1B_1A_1B_1A_2$ pentad described above (8.095 ppm resonance).

It is important to note that alcoholysis and midchain transreaction can now be spectroscopically differentiated. Alcoholysis can be identified by the disappearance of the 8.065, 4.231, and 3.423 ppm resonances, while midchain transreaction leads to the appearance of the terephthalate doublets of an AA′BB′ spin system. With the resonances of both midchain and alcoholysis transreaction identified, studies correlating the extent of transreaction to blend phase behavior can be conducted.

**Alcoholysis Transreaction.** The miscibility diagrams corresponding to the PEMPT B-OH/PC1 and PEMPT B-OH/PC2 blend series are shown in Figures 11 and 12, respectively. Details as to the construction of these diagrams have been reported in the second paper in this series.[1] For comparison, the miscibility diagrams of the PEMPT BNZ/PC1 and PEMPT BNZ/PC2 series of blends are also shown in Figures 11 and 12, respectively.[1] Replacement of the hydroxyl end groups by benzoate end groups prevents alcoholysis, while addition of DNOP prevents midchain transreaction. Thus, the PEMPT BNZ/PC homopolymer/homopolymer blends establish a baseline for the phase behavior prior to interchange reaction. The previously discussed $^1$H NMR results of the PEMPT 1B-OH/PC1 blend indicated that the DSC annealing/scanning program used for phase identification results in the quantitative reaction of the hydroxyl end groups of PEMPT via alcoholysis with PC. The absence of resonances corresponding to the terephthalate AA′BB′ spin system

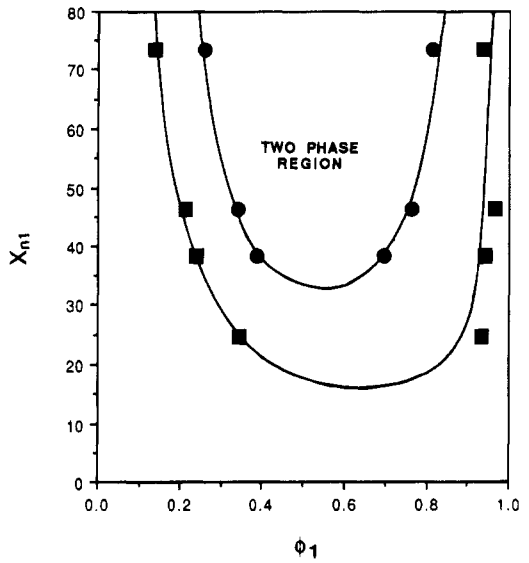


**Figure 12.** Miscibility diagram of DNOP-stabilized PEMPT B-OH/PC2 (●) and PEMPT-BNZ/PC2 (■) 50/50 blends. $X_{n1}$ is the number-average degree of polymerization of PEMPT and $\phi_1$ is the volume fraction of PEMPT.

indicates that no direct midchain reaction has occurred. Spectroscopic examination of other blends in these series—PEMPT 2B-OH/PC1, PEMPT 6B-OH/PC1, PEMPT 1B-OH/PC2, PEMPT 2B-OH/PC2, and PEMPT 6B-OH/PC2—yields the identical results. Thus, alcoholysis conversion is 100%, independent of the molecular weight of the blend components.

The miscibility diagrams of the PEMPT B-OH/PC blends represents the phase behavior after complete alcoholysis (Figures 11 and 12). Alcoholysis transforms the PEMPT B-OH/PC homopolymer/homopolymer blend into a PC–PEMPT–PC/PC triblock/homopolymer mixture. The significance of the alcoholysis reaction and the formation of triblock copolymers is apparent in Figures 11 and 12. Due to the formation of the triblock, the two-phase region of the PC–PEMPT–PC/PC blends is decreased considerably compared to that of the PEMPT BNZ/PC homopolymer mixtures. At typical commercial polyester molecular weights ($X_n$ > 70), shifts in the miscibility between the reacted and unreacted blends are significant along each branch of the curves. At equivalent molecular weights, the improved miscibility of diblock and triblock copolymers (as well as mixtures of these copolymers with pure homopolymers) compared to binary homopolymer blends is well documented.[22–26] The connectivity of the block and the emulsifying effect of the block copolymer in block/homopolymer blends lead to improved miscibility. These factors qualitatively explain the observed differences in phase behavior between the reacted and unreacted blends of Figures 11 and 12.

Quantitatively, the amount of alcoholysis required to shift the phase behavior from two phase to single phase can be determined from the degree of polymerization of PEMPT at the transition point (Figures 11 and 12). For a PEMPT B-OH/PC2 50/50 (w/w) blend, the degree of polymerization of PEMPT at the transition is 35 (Figure 12). Thus, at the transition from two-phase to single-phase behavior, ~5.7 mol % of the $A_1B_1$ repeat units of PEMPT are in the form of the $A_1B_1A_2B_2$ quartad of Figure 2b. Similar results are obtained for the PEMPT B-OH/PC1 blend.

**Simultaneous Midchain and Alcoholysis Transreaction.** Figure 13 shows the DSC traces of a PEMPT

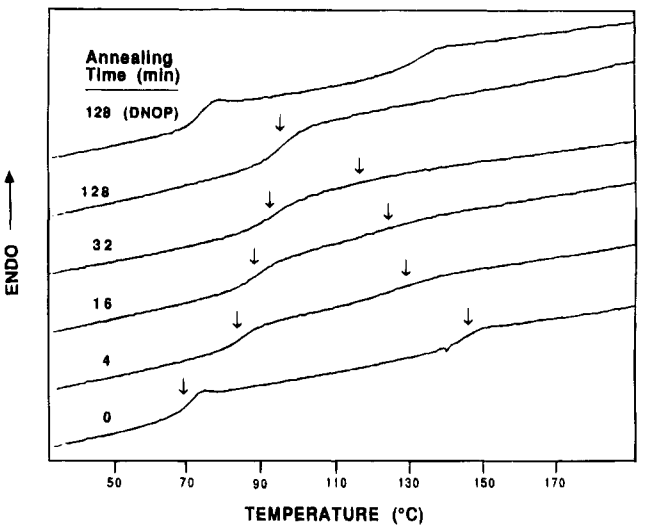


**Figure 13.** DSC heating scans of nonstabilized PEMPT 7-OH/PC2 blends annealed at 200 °C for the indicated times. Arrows indicate $T_g$ shifts.

**Table 4. GPC Data of Nonstabilized PEMPT 7-OH/PC2 50/50 Blends after Annealing at 200 °C for the Indicated Times**

| annealing time (min) | $M_n$ | $X_w/X_n$ | $X_z/X_w$ |
|---|---|---|---|
| 0 | 20 300 | 2.10 | 1.61 |
| 8 | 38 000 | 2.25 | 1.55 |
| 32 | 40 200 | 2.26 | 1.55 |
| 128 | 35 300 | 2.28 | 1.73 |

7-OH/PC2 nonstabilized blend annealed for times varying from 0 to 128 min. After 4 min, a notable shift in both the upper and lower $T_g$s is seen. By 32 min, there has been a large shift in the $T_g$s of both phases. After 128 min of annealing, the single sharp $T_g$ indicates a single-phase blend has been formed. The improvement in miscibility could be caused by several factors including solvent/preparation effects, molecular weight reduction (due to hydrolysis), or interchange reaction. The DSC trace of a DNOP-stabilized PEMPT 7-OH/PC2 blend annealed 128 min at 200 °C is shown to indicate the two-phase nature of the blend at equilibrium. From this and the previously discussed phase behavior studies, solvent/preparation effects cannot be the cause of the observed phase change. If hydrolysis is responsible, molecular weight changes should be apparent. GPC results of samples annealed for 8, 32, and 128 min show a considerable increase in $M_n$ compared to an as-precipitated sample (Table 4). From the miscibility diagrams on the PEMPT BNZ/PC2 blends (Figure 12), a decrease in molecular weight of PEMPT by at least a factor of 2 (easily identifiable by GPC) would be required to justify the observed improvement in miscibility. Combining these facts, one must conclude that the change in the phase behavior of the blend with annealing time is due to reaction between blend components.

Proton NMR spectra of the terephthalate and backbone methylene regions of DSC samples annealed 0, 4, and 8 min are shown in Figures 14a–c and 15a–c, respectively. In the samples annealed for 4 and 8 min, the resonance associated with the terminal terephthalate ring, 8.065 ppm, is replaced with a resonance (shoulder) at 8.095 ppm (Figure 14). This indicates alcoholysis has occurred (nearly quantitatively) during the short annealing time. The methylene backbone region of the spectrum (Figure 15) confirms these results, with the disappearance of the 4.231 ppm singlet and the 3.423 ppm multiplet (multiplet is barely visible

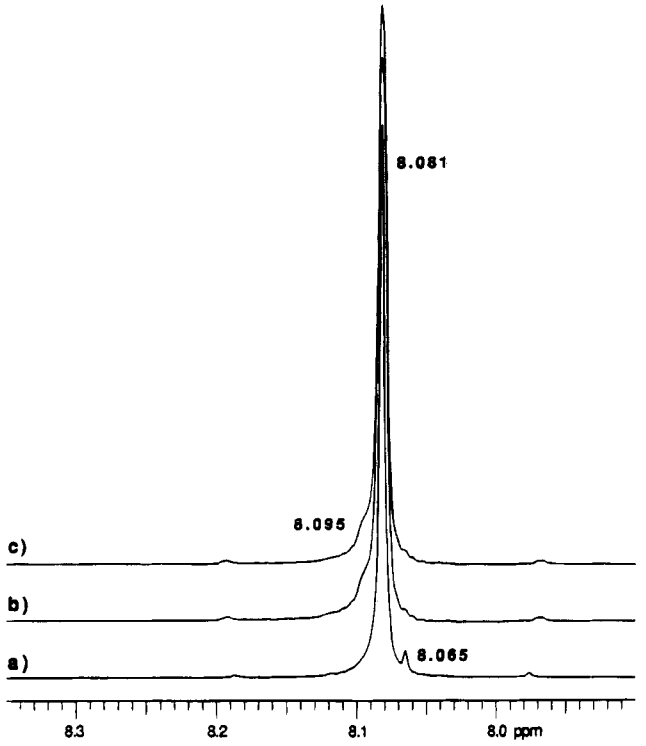


**Figure 14.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed at 200 °C for (a) O, (b) 4, and (c) 8 min. The terephthalate region of the spectrum is displayed.

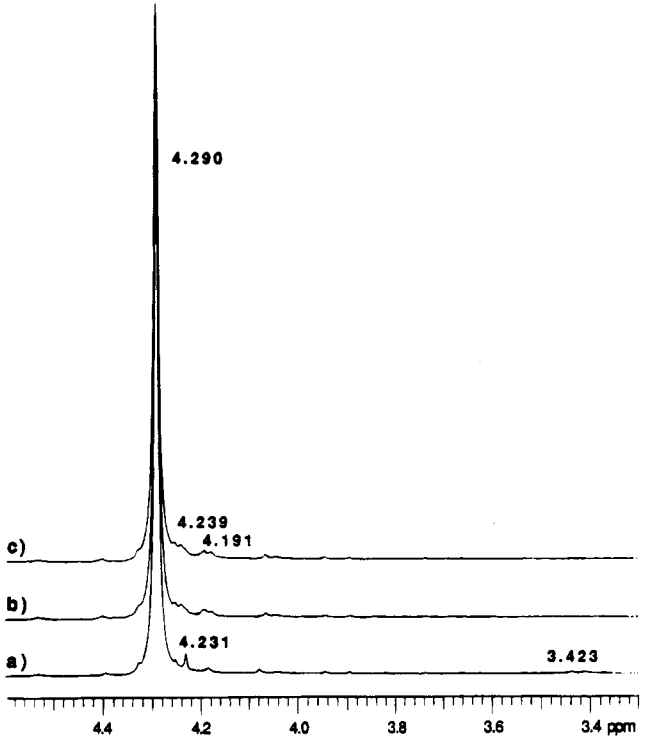


**Figure 15.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed at 200 °C for (a) O, (b) 4, and (c) 8 min. The methylene backbone region of the spectrum is displayed.

in Figure 15a). The GPC results of Table 4 also confirm these results. The GPC detector predominantly identifies the polyester. Thus, the large jump in the $M_n$ between unannealed sample and the sample annealed 8 min reflects an increase in the molecular size of the PEMPT chains as PC blocks are added to their ends. Overall, the initial $T_g$ shifts observed after 4 min of

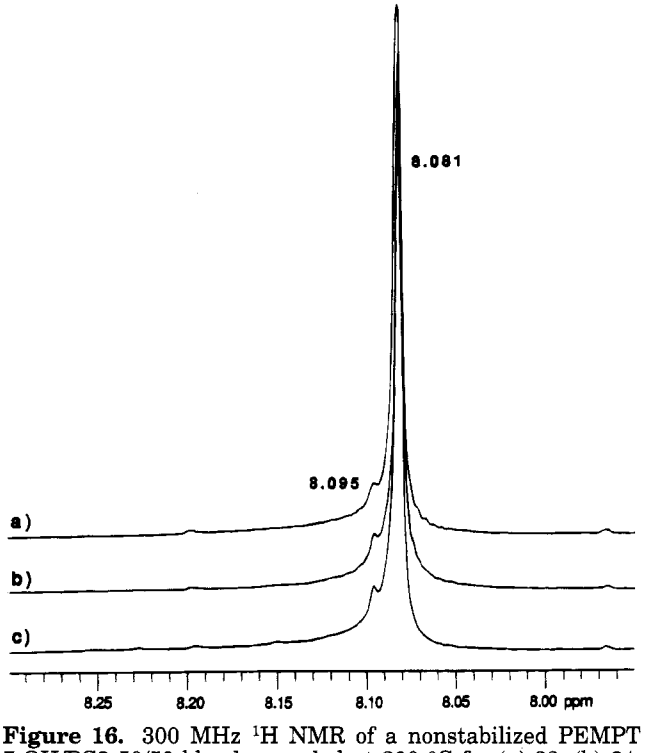


**Figure 16.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed at 200 °C for (a) 32, (b) 64, and (c) 128 min. The terephthalate region of the spectrum is displayed.

annealing (Figure 13) can be attributed to alcoholysis.

Continuing to longer annealing times, Figure 16 shows the terephthalate region of the $^1$H NMR spectra for samples annealed for 32, 64, and 128 min. The resonance at 8.095 ppm increases with annealing time, corresponding to the formation of the $A_1B_1A_2B_2$ quartad. The sample annealed for 128 min also shows the faint appearance of the pair of doublets (8.255, 8.227, 8.121, and 8.150 ppm) previously associated with direct midchain transreaction. These results are confirmed by the increase in intensity of the methylene proton resonances, 4.239 and 4.191 ppm, of Figure 17. Comparing the DSC scans of Figure 13 to the $^1$H NMR spectra of Figures 16 and 17, it is obvious that a small amount of interchange reaction has led to the transition from a two-phase to a single-phase blend.

A quantitative measure of the amount of interchange reaction leading to the phase transition can be made from the area ratios of the 4.239, 4.191, and 4.290 ppm resonances. From these ratios, it is determined that ~4 mol % of the propylene/terephthalate groups have been transformed into the $A_1B_1A_2B_2$ quartad sequence represented in Figures 1b and 2b. This value can be divided between the amount of alcoholysis and midchain transreaction. With alcoholysis being quantitative, the percentage of quartad sequences that formed via alcoholysis can be determined from the $M_n$ of the polyester. The $M_n$ of PEMPT 7-OH is 17 700, which corresponds to an $X_n$ of 71. The percentage of end groups in the polymer is 2.8. Thus, ~2.8% of the $A_1B_1A_2B_2$ quartads resulted from alcoholysis and 1.2% resulted from midchain reaction.

**Interpretation of Phase Transition Data.** The improvement in miscibility caused by interchange reaction is assumed to be associated with two main factors, the decrease in the molecular weight of the component polymers as transreaction occurs and the connectivity effect associated with the formation of block copolymers.

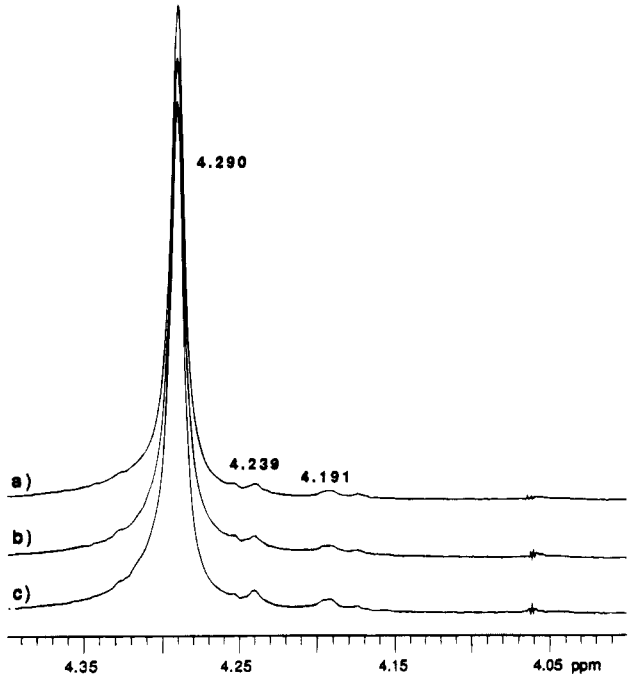


**Figure 17.** 300 MHz $^1$H NMR of a nonstabilized PEMPT 7-OH/PC2 50/50 blend annealed at 200 °C for (a) 32, (b) 64, and (c) 128 min. The methylene backbone region of the spectrum is displayed.

With this as a basis, two simple models of the transreacting blend will be used to theoretically justify the above results. The first model assumes that transreaction only leads to a decrease in the molecular weight of the polyester. The decrease in the molecular weight of PC and the connectivity effects will be ignored. With this assumption, the phase behavior studies of PEMPT BNZ/PC blends can be used to determine the extent of transreaction required to cause the phase transition. From Figure 12, the degree of polymerization of a PEMPT BNZ/PC2 50/50 (w/w) blend at the transition between single-phase and two-phase behavior is ~17. This implies that if the molecular weight of the polyester is lowered from the original $X_n$ of 71 to a value of 17, a single-phase blend will result. To lower the $X_n$ of PEMPT 7-OH from 71 to 17 would require 3–4 reactions per molecule (if the reactions are assumed to occur in the middle of the chain and the subsequent chain segments). This corresponds to ~4–6% interchange reaction. The molecular weight reduction of PC and the connectivity effects are both expected to improve the blend miscibility, lowering this value. The fact that transreaction occurs randomly along the chains and not selectively in the middle, as assumed, is expected to raise this value.

The second model comes from the diblock copolymer theories developed over the past two decades.[22-40] From these theories, the dominant parameter used to correlate the microphase separation transition to physical characteristics of the polymer is $(\chi N)$, where $\chi$ is the interaction parameter and $N$ is the number-average degree of polymerization of the block copolymer. In this model, the transreacting blend will be treated as an ideal block copolymer. It is assumed that each chain has undergone one midchain reaction exactly in the middle of both molecules to produce a perfect diblock. Polydispersity effects will also be ignored. PEMPT 7-OH and PC2 have degrees of polymerization of 71 and 85, respectively. This leads to a block copolymer with a DP of 78. The interaction parameter of the PEMPT/PC blend was previously calculated to be 0.044.[1] With these two values, $(\chi N)$ for the model PEMPT/PC2 diblock is 3.4. For a given block composition, Leibler has determined the values for the above product at the microphase separation transition point, $(\chi N)_s$.[25] A block copolymer is predicted to be miscible if $(\chi N) < (\chi N)_s$. For the current model system, $(\chi N)_s$ is ~12.[25] Thus, with $(\chi N) < (\chi N)_s$, the model PEMPT/PC block copolymer would be expected to form a single-phase blend. This model diblock system is based on a single transreaction per chain which corresponds to ~3.0 mol % of the $A_1B_1$ repeat units of PEMPT transformed into the $A_1B_1A_2B_2$ quartad. Once again the assumption of interchange reaction occurring exactly in the middle of the chains is too restrictive. Transreaction is expected to proceed randomly along the chains, and this fact will likely increase the level of reaction required to form a miscible blend over the value predicted here. Additionally, kinetic and diffusion factors are also expected to increase the extent of transreaction required for the phase transition.

Although the two interpretations given above represent an oversimplified version of the transreacting blend, the analysis is useful in that it defines a range where the true value is expected to lie. The experimentally determined value for extent of transreaction required to cause the phase transition, 4%, falls between the values calculated from these model systems, adding theoretical support to the experimental findings. Additionally, the value of 5.7% reaction at the transition point, determined from the blends undergoing only alcoholysis exchange reaction (Figures 11 and 12), is also in fair agreement with the above results.

## Conclusions

Spectroscopic examination of a transreacting PEMPT/PC blend enables the simultaneous monitoring of midchain and alcoholysis reaction. Alcoholysis reaction can be identified by the disappearance of resonances corresponding to end-group structure of PEMPT. Resonances associated with both the methylene and aromatic segments of the end group can be monitored. Midchain transreaction can be followed via the formation of a nonsymmetrically substituted aromatic ring in PEMPT. This structure produces a distinct resonance pattern in both 1-D and 2-D $^1$H NMR spectra.

Although it cannot lead to complete randomization of the blend, alcoholysis causes significant changes in the phase behavior of PEMPT/PC blends. Transformation of the original binary blend to a triblock/homopolymer mixture enhances miscibility in qualitative agreement with theory. The fact that alcoholysis of PC by PEMPT end groups is quantitative supports previous claims that alcoholysis of polyesters by phenol end groups of PC does not occur.[2] If such a reaction did occur, an equilibrium level of hydroxypropylene groups should be reached and detected by $^1$H NMR. No such equilibrium level is observed in any of the PEMPT/PC blends analyzed.

A two-phase PEMPT/PC blend, undergoing both midchain and alcoholysis interchange reaction, is transformed into a miscible blend after 4 mol % of the $A_1B_1A_2B_2$ sequence is formed. Of this 4.0%, 2.8% is due to alcoholysis and 1.2% corresponds to midchain transreaction. This result qualitatively agrees with predictions based on simple models of the transreacting blend. At the phase transition, the blend is a multiblock copolymer, far from complete randomization. In these

nonstabilized blends, alcoholysis exchange reaction is nearly quantitative after annealing 4 min at 200 °C. This suggests that, unless alcoholysis can be inhibited, blends of this nature will become mixtures of triblock copolymers and the original homopolymers at the temperatures and times commonly used for melt processing.

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