

Block Copolymer Formation from the Melt Reaction Between Polycarbonate and Poly(ethylene-co-butylene) Diol

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ABSTRACT: The block copolymer formation from the exchange reaction between polycarbonate (PC) and poly(ethylene-co-butylene) diol (POH) occurring during melt mixing was studied. The exchange reaction proceeded by the attack of active chain ends of hydroxyl-terminated POH on the inner carbonate groups of PC. The reaction was accelerated in basic condition in the presence of a hindered amine. The formation of block copolymer was confirmed by $^1\text{H-NMR}$ analysis. The proceeding of the exchange reaction was analyzed with UV spectrometry by measuring the absorbance at 285 nm of the less-reactive phenolic end group of PC oligomers produced. The reaction was terminated when the hydroxyl end groups of POH were completely consumed. It was found from the analyses by GPC and DSC that the exchange reaction between PC and POH takes place rather uniformly by random scission of the chain. The block copolymer obtained here will be employed as a compatibilizer of PC/polyolefin blends in a future study. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1725–1732, 2001

Key words: reactive mixing; polymer blends; block copolymer; polycarbonate

INTRODUCTION

In recent years considerable interest has arisen in the study of reactive blending of several polymers or of the exchange reaction that may occur during the melt-mixing process^{1–12} because it is possible to acquire from the reaction a product that has commercial potential. The block copolymer obtained during the melt reaction can play the role of compatibilizer in an incompatible blend system. The exchange reaction may proceed by two different mechanisms,^{13–15} depending on the location of reactive functionalities within polymer chains: (1) a direct exchange reaction between

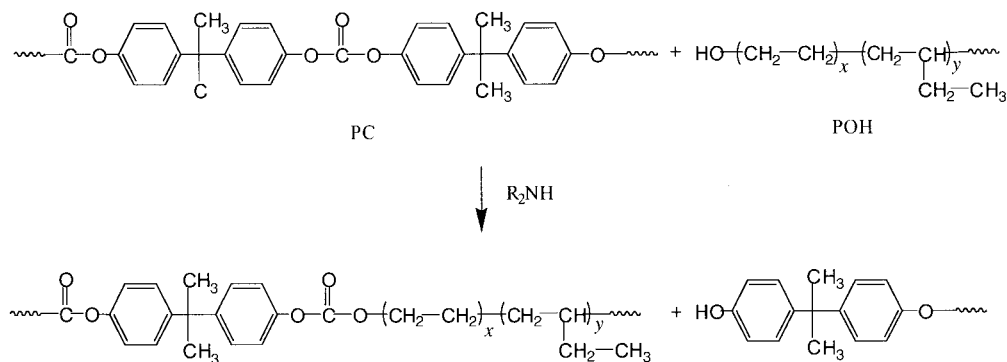
inner functional groups located in the main backbone of polymer chains or (2) by the attack of reactive functional groups at chain ends on inner groups.^{9–12}

The exchange reaction between the end-capped polycarbonate (PC) and the hydroxyl or carboxyl reactive groups in polyesters was investigated to verify the mechanism of reaction between active chain ends and inner functional groups.¹³ Several workers previously studied the processing characteristics of PC and nylon 6 blends,^{16–18} arguing that the reaction occurs only by amino terminals on the inner carbonate groups during melt mixing at 240°C, whereas the reaction of the inner amide group and the inner carbonate group occurs above 300°C.

We were interested in the system in which an exchange reaction is induced by active chain ends

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Scheme 1

in the blend of poly(ethylene-*co*-butylene) diol (POH) and commercial PC end-capped with tertiary butyl phenolate as the molecular controller. The purpose of the reaction in our study was to modify the PC chain with the nonpolar and flexible chain segment. The PC block copolymer modified with aliphatic chain will be employed in a subsequent study as a compatibilizer of immiscible blends including the polar and nonpolar polymers such as the PC and polyolefin blend.

In the reactive mixing of the POH and PC blend, the carbonate group of PC becomes involved in the alcoholysis process and exchange reaction with the hydroxyl group of POH. The exchange reaction at melt occurs with the attack of active hydroxyl terminal groups on the inner carbonate groups, the reaction of which is shown in **Scheme 1**. In this report we mainly focused on the interchain reaction and the formation of block copolymer examined using UV, NMR, and so forth.

EXPERIMENTAL

The bisphenol-A polycarbonate (PC) used was molding grade (supplied by Samyang Inc., Korea), having a weight-average molecular weight (M_w) of 25,000 g/mol [PI (polydispersity index) = 2.1]. The poly(ethylene-*co*-butylene) diol (POH; Mitsubishi Chemical Co., Japan) had a number-average molecular weight (M_n) of 2450 g/mol. The polymers were separately dried in vacuum at 110°C to prevent hydrolysis prior to melt mixing. The hindered amine used as a catalyst was poly[[6-[1,1,3,3,-tetramethyl-butyl]amino]-1,3,5-triazine-2,4-diy]][(2,2,6,6-tetramethyl-4-piperidiny]imino]-

1,6,-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny]imino)] (Ciba Specialty Chemicals, Summit, NJ). The hindered amine that we chose is a secondary amine to be most effective for hydrolysis of PC.¹⁹

Reactive mixing was carried out under nitrogen purge in a Brabender mixer operating at 45 rpm and 280°C. The premixed or unpremixed samples of the PC and POH (1/1 mol/mol) were added to the mixer. The mixing temperature was determined for the polymers so as to expose them to an optimal reaction condition. The samples were taken out from the mixer after the reaction times for 5, 10, 20, 40, 60, and 80 min elapsed, respectively. The premixing was performed in a twin-screw extruder ($d = 40$ mm; $L/D = 36$; 250 rpm) at 270°C.

The UV spectra were recorded using a Shimadzu UV-2100S spectrometer (Shimadzu Corp., Japan) of 0.002 wt % chloroform solution by measuring the absorbance at 285 nm. The ¹H-NMR spectra were measured on a Varian 200 FT-NMR spectrometer (Varian Associates, Palo Alto, CA) at room temperature using deuterated chloroform as a solvent and tetramethylsilane as a standard. The GPC analysis was carried out using a Waters GPC 2690 (Waters Instruments, Rochester, MN). The tetrahydrofuran solution of PC and POH was prepared. The instrument was calibrated using the polystyrene calibration standard. The thermal properties of the blends were measured with Perkin-Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT). All measurements were made at a scan rate of 10°C/min within a temperature range from room temperature to 300°C, and the glass-transition temperature (T_g) was taken as the temperature of the half-height of the transition in heat-flow curves. The melt fluidity was

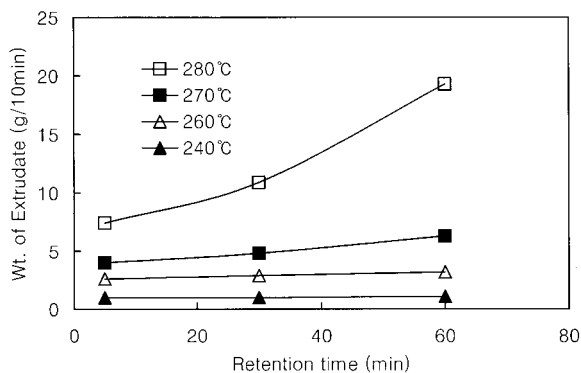


Figure 1 Mass of the PC/POH (1/1 mol/mol) melts extruded for 10 min after retention at various temperatures. Temperatures of retention are indicated in the figure.

measured using an extrusion plastometer (Ceast 6841, Italy). For all samples, the pressure applied was $P = 1.2 \text{ kg/cm}^2$. The melts extruded for 10 min were weighed after retention for various periods at temperatures ranging from 240 to 280°C. Prior to measurement, the samples were dried at 120°C for 4 h.

RESULTS AND DISCUSSION

The reaction temperature is a major factor influencing the intermolecular exchange reaction.^{9–12} In the melt mixing of polymers containing reactive functional groups (such as carbonate, ester, amide, etc.) the end-group-activated or catalyst-activated exchange may occur below 300°C,^{1–8} whereas the thermally activated exchange or thermal degradation occurs above 300°C.^{9–12} At lower temperatures, the reaction does not occur efficiently because of the lack of the chain mobility as well as the deficiency of the activation energy for the reaction. At too high a temperature, the interchain reaction is surpassed by thermal decompositions.

In the system of reaction between active ends and inner functional groups, such as the PC/POH blend, the reaction proceeds by attack of the reactive end groups of POH on the PC chains, yielding the block copolymer and the short chain of PC ended with fewer reactive phenol groups. The interchain reaction may be characterized by either the reduction of PC chain length or the broadening of chain length distribution, which consequently leads to an increase of melt fluidity. In

Figure 1, the mass of the melt extruded for 10 min is shown as a function of the retention time. As retention time increases, the melt fluidity of the PC/POH blends does not noticeably change, which suggests that the interchain reaction does not occur at temperatures lower than 270°C. The melt fluidity increases abruptly at 280°C, at which the chemical transformation between the POH and PC appears to occur, given that the melt fluidity of the PC itself was not changed at the same condition in a separate experiment. At higher temperature, the considerable change of the melt fluidity was observed resulting from radical thermal decomposition. In other words, the interchain reaction becomes thermally activated above 280°C. The reactive mixing of the PC/POH blend was carried out at 280°C in this study.

For the interchain reaction of equimolar PC/POH blends, the carbonate groups were hydrolyzed by reacting with the hydroxyl groups of POH, and decomposed to form equimolar phenolates and the block copolymer (as shown in **Scheme 1**). For the direct exchange of inner functional groups, the catalysts for acidolysis, esterolysis, or transesterification may be needed below 300°C,⁷ whereas the reaction involving the active chain ends does not generally require catalysts. The latter is the case in this study, as shown in Figure 1.

The diphenyl carbonate is hydrolyzed in either an acidic or an alkaline condition, but more radically in an alkaline condition. It was also reported that the hydrolysis of PC was accelerated in weak bases such as hindered amines. A secondary hindered amine was employed as a catalyst to

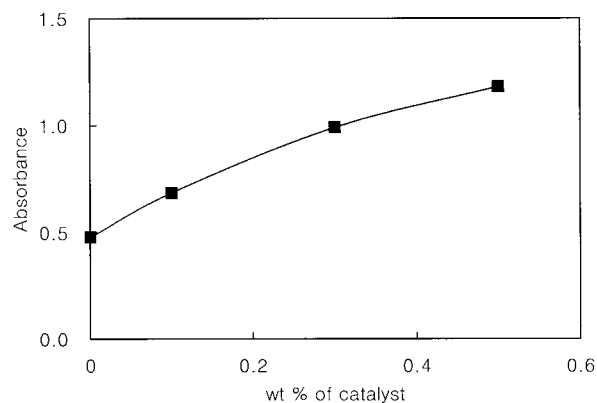
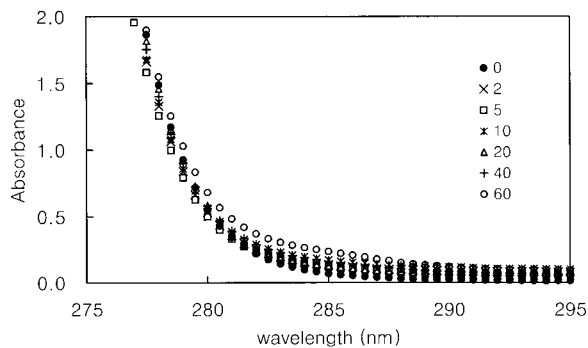
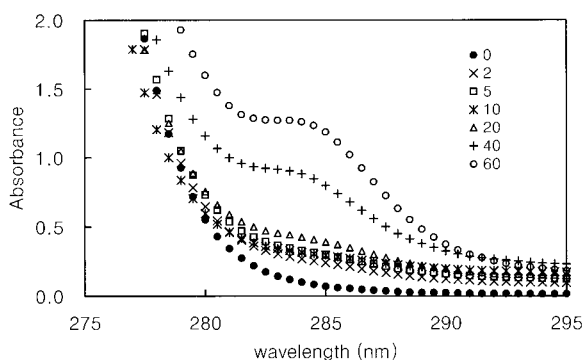


Figure 2 UV absorbance of the PC/POH (1/1 mol/mol) blends at 285 nm as a function of hindered amine added. The blends were mixed at 280°C for 60 min.



(a)



(b)

Figure 3 UV absorbance of the PC/POH (1/1 mol/mol) blends (a) without premixing and (b) with premixing during melt mixing. The mixing times (min) are indicated in the figure.

promote the exchange reaction and to control the reaction time.¹⁹ In Figure 2, the absorbance of the mixtures at 285 nm in UV spectra is shown as a function of the weight fraction of the hindered amine. Each sample was mixed for 60 min at 280°C. The absorbance is assigned to the phenolic groups of PC oligomers, which is less reactive than the hydroxyl OH of polydiol. Its increase indicates the formation of the block copolymer of higher yield.

The UV absorbance spectra of PC/POH blends are shown in Figure 3(a) and (b), without or with the hindered amine, respectively, which were recorded from the blends taken out at different time intervals of mixing up to 60 min. Because of the immiscibility of the PC and POH, a severe phase segregation definitely hindered the homogeneous mixing of both polymers at the initial stage of

mixing. As the mixing continued, the phases developed into smaller droplets by shear and the melt reaction proceeded at the interfaces. In the presence of the hindered amine, the absorbance at 285 nm increased rapidly. It is evident that the attack of the hydroxyl end group in POH on the inner carbonate group causes the block copolymer and the PC oligomer to end with phenoxy groups. The composition of the block copolymer formed at the initial stage depends on the molecular size of the polymers used for reactive mixing. We used the PC of $M_w = 25,000$ g/mol ($PI = 2.1$), approximately fivefold larger in number-average molecular weight than the hydroxyl-terminated POH of 2450 g/mol. The initial block copolymer subsequently includes the higher composition of carbonate units, when the mechanism of the reaction is taken into consideration.

In a later stage, the copolymer should approach equimolar composition and the PC homo-oligomers with phenoxy groups are produced as a by-product. This type of exchange reaction terminates with the consumption of reactive chain ends,¹³ that is, when the hydroxyl end groups are exhausted from the reaction with the carbonate inner functional groups. To examine the effect of premixing, the UV spectra of the premixed or unpremixed blends were analyzed, and the absorbance at 285 nm is shown in Figure 4(a) and (b). The phase segregation initially inhibits inter-chain reaction because the contact of the reactive sites is restricted only at the interfaces of macroscopically separated phases. Apart from premixing, the blend without the hindered amine shows no prominent increase of absorbance up to a mixing time of 60 min. The blend containing the 0.5 wt % hindered amine shows a relatively slow increase of absorbance, which continues until the mixing time reaches 20 min, after which time the peak increases rapidly to 1.2 by absorbance, where the effect of initial phase separation is diminished. With premixing, the blends show an overall gradual increase of absorbance [Fig. 4(b)]. The absorbance after mixing for 60 min is almost the same for either of the blends containing the hindered amine with or without premixing. For the blends without catalyst, the absorbance of premixed blends is three times higher than that of unpremixed blends. It suggests that the effect of premixing becomes more significant for the blend without the catalyst.

To confirm the formation of the block copolymer, the ¹H-NMR spectra were analyzed for the

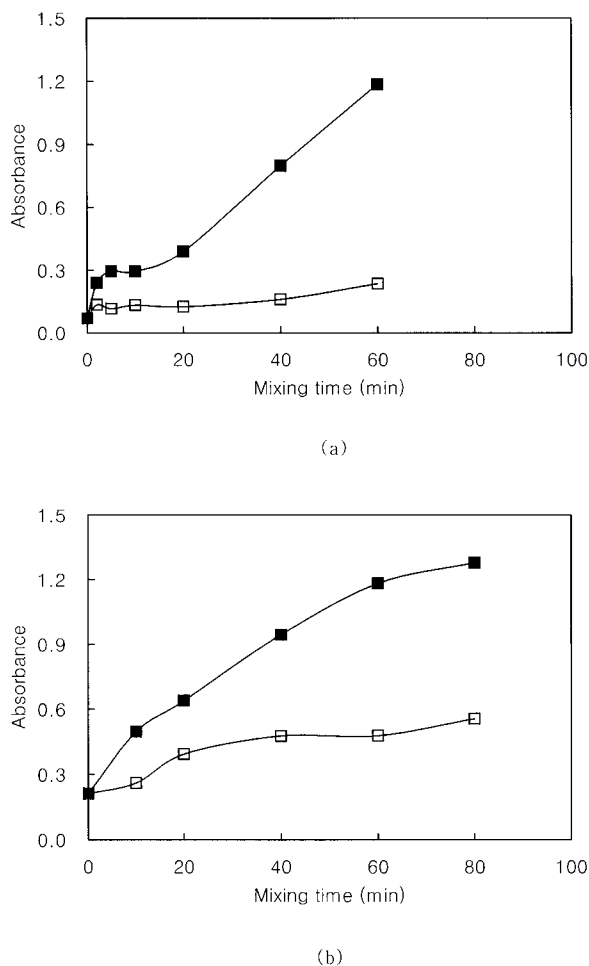


Figure 4 UV absorbance at 285 nm of PC/POH (1/1 mol/mol) blends (a) without premixing and (b) with premixing during melt mixing at 280°C. Filled squares indicate the mixtures reacted in the presence of catalyst; open squares indicate the mixtures reacted in the absence of catalyst.

mixtures taken out after mixing for 0, 40, and 60 min, respectively,²⁰ the results of which are shown in Figure 5(a) and (b). The major peaks of protons are from three major groups: (1) the methyl protons of bisphenol-A of PC, detected around 1.67 ppm, or the methyl protons of aliphatic POH not adjacent to OH groups, appearing at 1.27 ppm; (2) the phenyl proton of PC, detected at 7.23 ppm [Fig. 5(a)], which are not affected in chemical shift by the concurrent reaction; and (3) the α -hydrogens of aliphatic POH, whose concentration is minimal because it is located adjacent to the chain end functionality. The enlarged peaks of the protons are shown typically at 3.6 ppm (peak B), as shown in Figure 5(b). When the

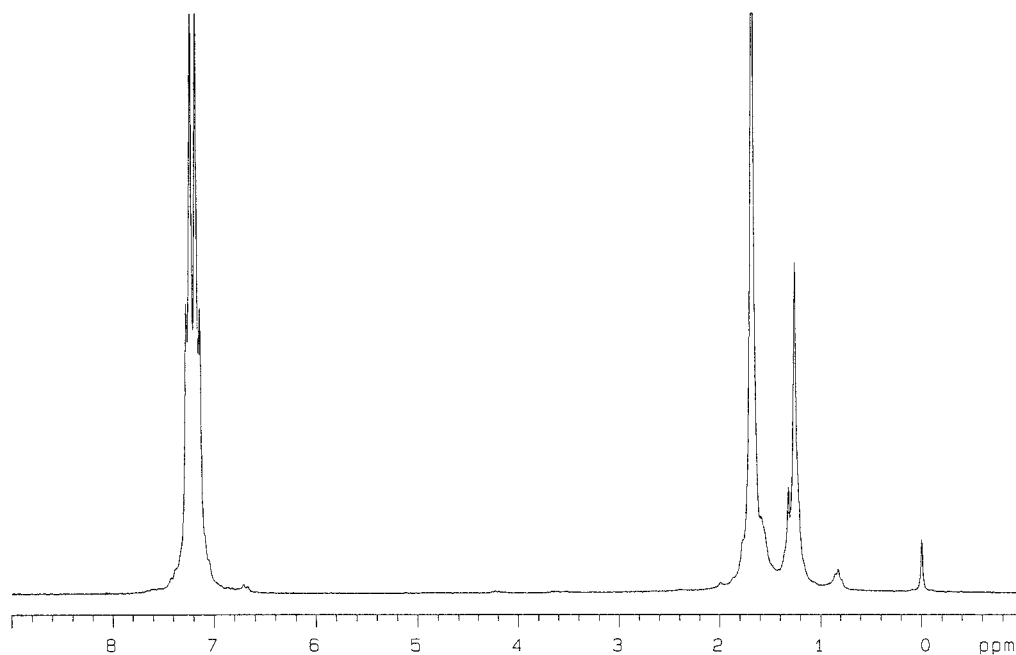
reaction proceeds between PC and POH, there occurs the shift of peaks. The figure shows enlarged peaks at 4.2 ppm (peak A), assigned to the resonance of the protons of carbon next to the carbonate group created from heat-induced reactions between PC and POH during mixing.

In the reaction containing active chain ends, the reaction proceeds until the functionality of chain ends is consumed completely. It was subsequently confirmed that the aliphatic POH is completely combined with PC molecules when mixed for 60 min at 280°C. The formation of block copolymers with the scission of PC chains drives the viscosity of the system in an upward direction, whereas the degradation reduces the melt viscosity. The reduction is attributed to the PC short chains formed concomitantly during the reaction. In this case, the PC reacting through carbonate groups undergoes a random scission process, and the molar mass of the PC homo-oligomers should vary according to the random scission law.

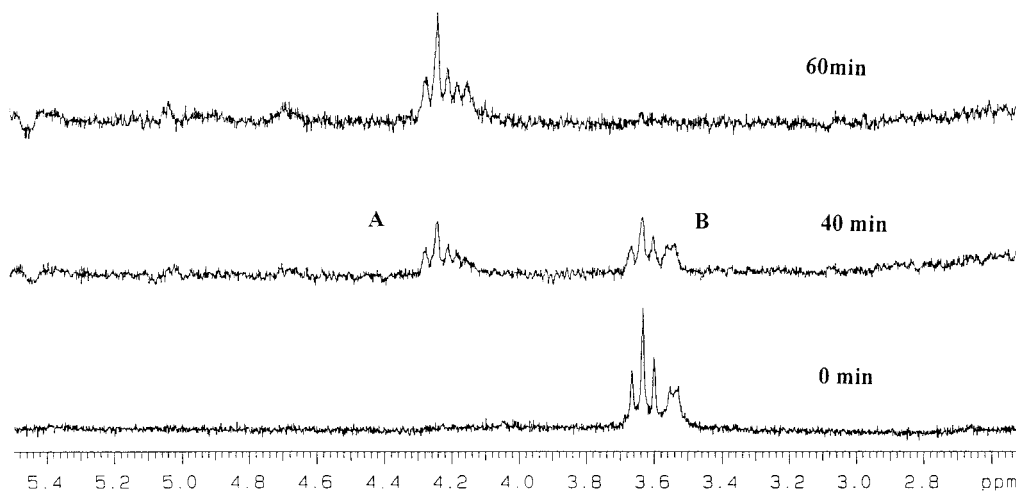
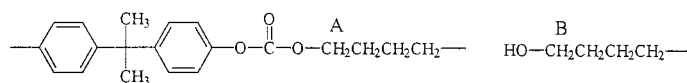
Figure 6 shows the change of T_g of the PC phase in the PC/POH (1/1 mol/mol) blend according to repeated scans in the range from room temperature to 300°C. The T_g of the POH phase was not detected because the POH should have a significantly lower T_g than the range we explored for measurement. The T_g decreases as the scan number increases. The reduction of T_g suggests that the scission takes place randomly along the chain by the effect of chemical attacks during cycled heating.¹⁴ The decrease of T_g also stems from the enhanced compatibility of two phases composed of PC and POH by the block copolymer formed. The reaction was intended to modify the PC by endowing it with flexibility and reducing its hydrophilicity.

To analyze thermal behaviors of the blends as the interchain reaction proceeds, DSC was carried out for the premixed blends containing 0.5 wt % catalyst. Figure 7 shows the plot of T_g of the PC phase as a function of mixing time. The T_g declines gradually as mixing time increases because the PC becomes involved in a chain scission during melt mixing and the block copolymer or homo-oligomers are yielded through the reaction.

Figure 8 shows the summary of the change on the molecular weight of the PC/POH blends during melt mixing. The molecular weight of PC/POH blend decreases, whereas the molecular weight distribution is almost constant during mixing, which suggests that the exchange reaction between POH and PC occurs with statistical



(a)



(b)

Figure 5 (a) ^1H -NMR peaks of PC/POH (1/1 mol/mol) blends containing 0.5 wt % hindered amine after melt mixing at 280°C , and (b) shift of enlarged peaks caused by the exchange reaction. The mixing times are indicated in the figure.

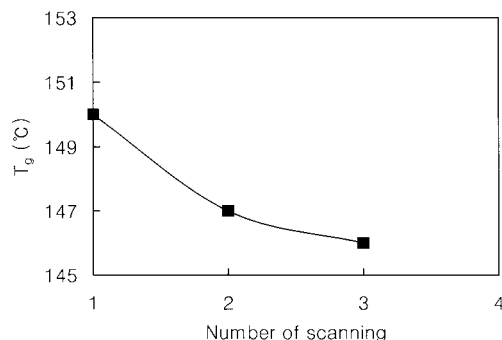


Figure 6 T_g of PC/POH (1/1 mol/mol) blends on repeated thermal scanings in nitrogen. Heating rate was 10°C/min and cooling rate was 30°C/min.

distribution.¹⁴ The reduction of molecular weight of blends containing the catalyst was greater than that of blends without the catalyst. For example, the molecular weight of blends containing catalyst after reactive mixing for 20 min is almost same as that of blends containing no catalyst after mixing for 60 to 80 min. The result is coincident to the trend of concentration of the phenol group by UV spectrometry during melt mixing. It suggests that an alcoholysis reaction takes place during melt mixing in **Scheme 1**. We found that the rate of the exchange reaction without catalyst is quite slow.

CONCLUSIONS

For the exchange reaction of polycarbonate and aliphatic polydiol, it was confirmed that the reac-

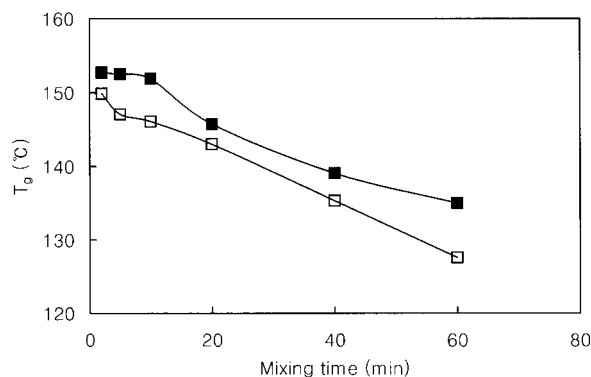


Figure 7 Plot of T_g 's of unpremixed PC/POH (1/1 mol/mol) blends as a function of mixing time at 280°C. Filled squares indicate the first scan of thermal heating and open squares indicate the second scan. Heating rate was 10°C/min.

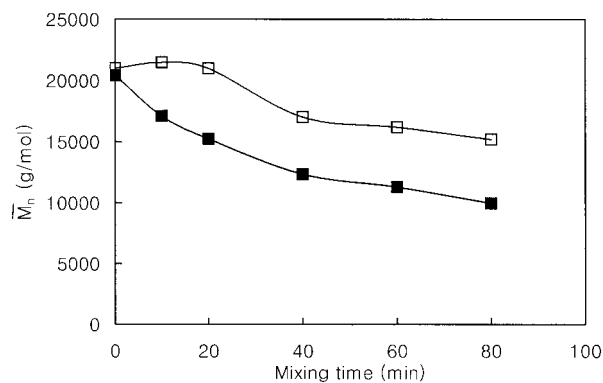


Figure 8 Plot of molecular weight of premixed PC/POH (1/1 mol/mol) blends as a function of mixing time during melt mixing at 280°C. Filled squares indicate the mixtures reacted in the presence of catalyst; open squares indicate the mixtures reacted in the absence of catalyst.

tion occurs by the attack of active chain ends on the inner carbonate group. The GPC and DSC results show the decrease of the molecular weight of PC, resulting from chain scission by alcoholysis. We obtained evidence for the formation of block copolymer by ¹H-NMR spectra, where the POH is completely combined with PC when mixed for 60 min at 280°C. Using the phenol analysis by UV spectrometry, the extent of exchange reaction could be detected, and the effect of the hindered amine was qualitatively examined as a catalyst of the exchange reaction. It was determined that the melt reaction between the PC and POH is a good example of a reaction occurring through active chain ends. The block copolymer obtained will be used in various fields including the compatibilization of PC/polyolefin blends as well as PC modification.

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