



## Solid-state NMR Studies of Miscibility and Morphology in Blends of Bisphenol-A type Polycarbonate and Poly (ester-ether) Elastomer

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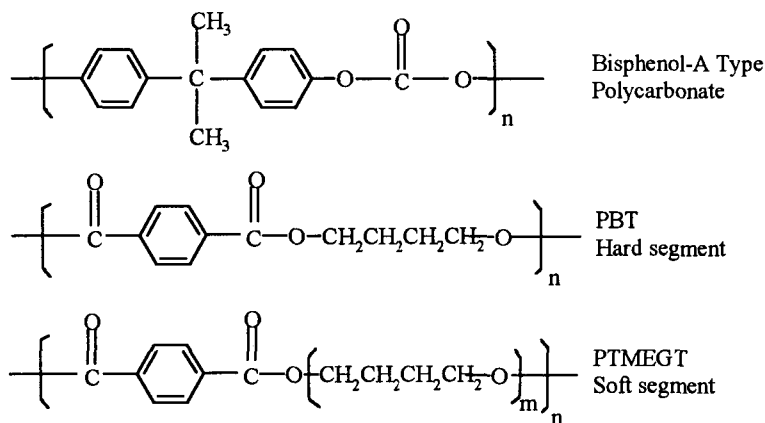
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**Abstracts:** Miscibility and morphology in blends of bisphenol-A type polycarbonate and poly (ester-ether) elastomer with different compositions are studied by solid-state NMR spectroscopy.  $^{13}\text{C}$  Solid-state NMR of CP/MAS/TOSS/DD, CP/MAS/DD, inversion recovery CP/MAS/DD, and 2D rotor driven spin diffusion techniques are used to identify the miscibility, morphology, and transesterification in blends. The blends of PC /PBT elastomer with 15% to 42% of soft segment seem to be single phase miscible mixing and those of PC/PBT and PC/PBT elastomer with 62% of soft segment are cocontinuous two phase immiscible mixing. No significant transesterification reactions are observed in blends with different compositions.

### INTRODUCTION

Bisphenol-A type polycarbonate(PC) is an amorphous and has a high glass transition temperature ( $T_g = 145^\circ\text{C}$ ,  $T_g$  is glass transition temperature) but its solvent resistance is very poor. So, blends of PC and other polymers are studied for many cases. Thermoplastic polycondensate with PC is characterized by an exceptional toughness (1-7). Thermoplastic elastomers that are used to blend with polycarbonate have a phase-separated microstructure and are showing balance properties of two components. These thermoplastic elastomers are block copolymers of poly (butylene terephthalate)(PBT) and poly (tetramethylene ether) glycol terephthalate (PTMEGT), so called poly- (ester ethers)(PEE). Fig. 1 shows the chemical structure of PC, PBT, and PTMEGT. The thermoplastic elastomer, PEE, consist of hard segment of PBT blocks and soft segments of PTMEGT blocks. Hard segments are crystalline state, high melting point( $220^\circ\text{C}$ ), and excellent solvent resistance. Soft segments are an amorphous state and result in a low  $T_g$  that gives low melting temperature and rubbery phases. Therefore, these PBT/PTMEGT block copolymers (PEE) are showing excellent mechanical strength and elastic properties over wide range of temperature (8, 9).

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**Fig. 1.** Chemical structures of bisphenol-A type polycarbonate (PC), poly (butylene terephthalate)(PBT), and poly (tetramethylene ether) glycol terephthalate (PTMEGT). Thermoplastic elastomer is a block copolymer of PBT and PTMEGT, so called poly- (ester ethers)(PEE).

Miscibility and morphology in blends of bisphenol-A type polycarbonate and poly (ester-ether) elastomer with different softsegment ratio are studied by solid-state NMR, liquid-state NMR, and FT-IR studies.

## EXPERIMENTAL METHODS

### *Materials :*

Five different kinds of sample were used to identify miscibility and morphology in blends of bisphenol-A type polycarbonate and poly (ester-ether) elastomer with different softsegment ratio. Blends of PC/PBT and PC/PEE were prepared by melt mixing in a twin-screw extruder with 0.3wt% stabilizer to prevent the transesterification during processing. The processing temperature of injection molding was at 230 °C and the residence time was approximately less than 1min. The composition of two components of PC/PBT and PC/PEE is 50/50 blend. (10).

Table 1 shows the thermal data of PC/PBT and PC/PEE blends by Differential Scanning Calorimeter (DSC)(10). The T<sub>c</sub> (crystalline temperature) and T<sub>m</sub> (melting temperature) of PEE containing 15, 30, 42, and 62 wt% of soft segment shifted remarkably to the lower temperature in the blends.

### *Solid-state NMR spectroscopy :*

Miscibility, morphology and transesterification reaction of these five blends can be studied by solid-state NMR spectroscopy. Experimental condition and pulse programs are in

**Table 1.** DSC data for PC/PBT and PC/PEE blends (10). A 72D means a block copolymer of 85% of PBT and 15% of PTMEGT. A 63D means a block copolymer of 70% of PBT and 30% of PTMEGT. A 55D means a block copolymer of 58% of PBT and 42% of PTMEGT. A 40D means a block copolymer of 38% of PBT and 62% of PTMEGT.

| 50/50 Blend of PC/PEE<br>(% of PTMEGT) | Cooling        | 2 <sup>nd</sup> heating |                |
|--|----------------|-------------------------|----------------|
|  | T <sub>c</sub> | T <sub>m</sub>          | T <sub>c</sub> |
| PC/PBT (None)                          | 178            | 223                     | --             |
| PC/72D (15%)                           | 161            | 217                     | --             |
| PC/63D (30%)                           | 147            | 210                     | --             |
| PC/55D (42%)                           | 122            | 191                     | --             |
| PC/40D (62%)                           | 96             | 170                     | --             |

Fig. 2. <sup>13</sup>C solid-state NMR spectra were measured at 75.4MHz on a Bruker DSX 300 MHz NMR Spectrometer with static magnetic field strengths of 7.05T, using a standard double bearing probehead. Samples were placed into 4mm diameter of zirconia rotor. Spectra were recorded using cross polarization with <sup>1</sup>H decoupling at the magic angle and suppressed spinning side band (CP/MAS/TOSS/DD), cross polarization with time delayed 1H decoupling at the magic angle (CP/MAS/DELAYDD), inversion recovery CP/MAS/DD, and 2D rotor driven spin diffusion experiments with 5 ~ 6.922 KHz spinning rate and recorded under room temperature.

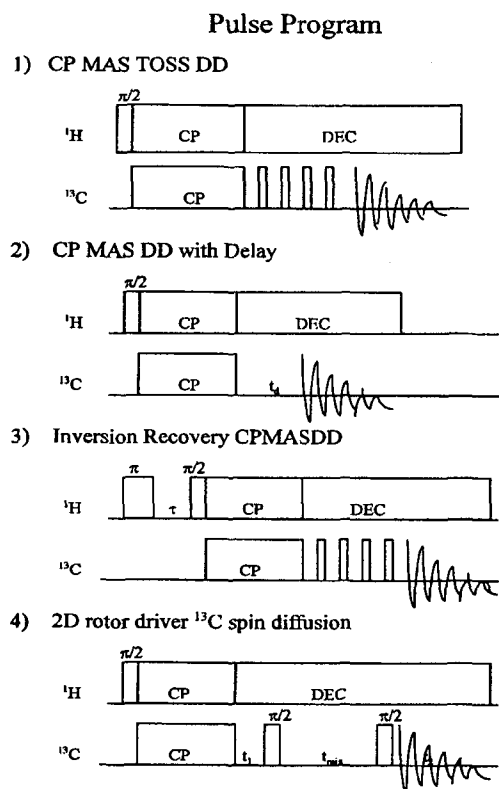
2D rotor-driven spin diffusion experiment is same as 2D exchange NMR in rotation solids (11). Magic angle was adjusted using <sup>79</sup>Br resonance of KBr at first, and the <sup>13</sup>C resonance of adamantane and glycine were used to assure the accurate setting. The chemical shifts are referenced to carbonyl chemical shift of glycine at 176.03ppm. Each chemical shift are assigned using spectral editing techniques and verified by solution NMR spectra.

#### *Liquid-state NMR spectroscopy :*

Transesterification Reaction of PC and PEE can be measured by solution-state nmr spectroscopy also. Experimental conditions are as below. Measurements <sup>13</sup>C liquid state NMR spectra were performed at 140.5MHz on a JEOL GSX 500 MHz NMR spectrometer with static magnetic field of 11.74T, using a standard carbon 5mm probe head at room temperature. 50% of deuterated methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>-d<sub>2</sub>) and 50% of deuterated trifluoroacetic acid (TFA-d<sub>1</sub>) were used as solvent.

#### *FT-IR :*

Transesterification Reaction of PC/PEE was studied by FT-IR spectroscopy also.



**Fig. 2.** A List of pulse program that are used to measure <sup>13</sup>C solid-state nmr

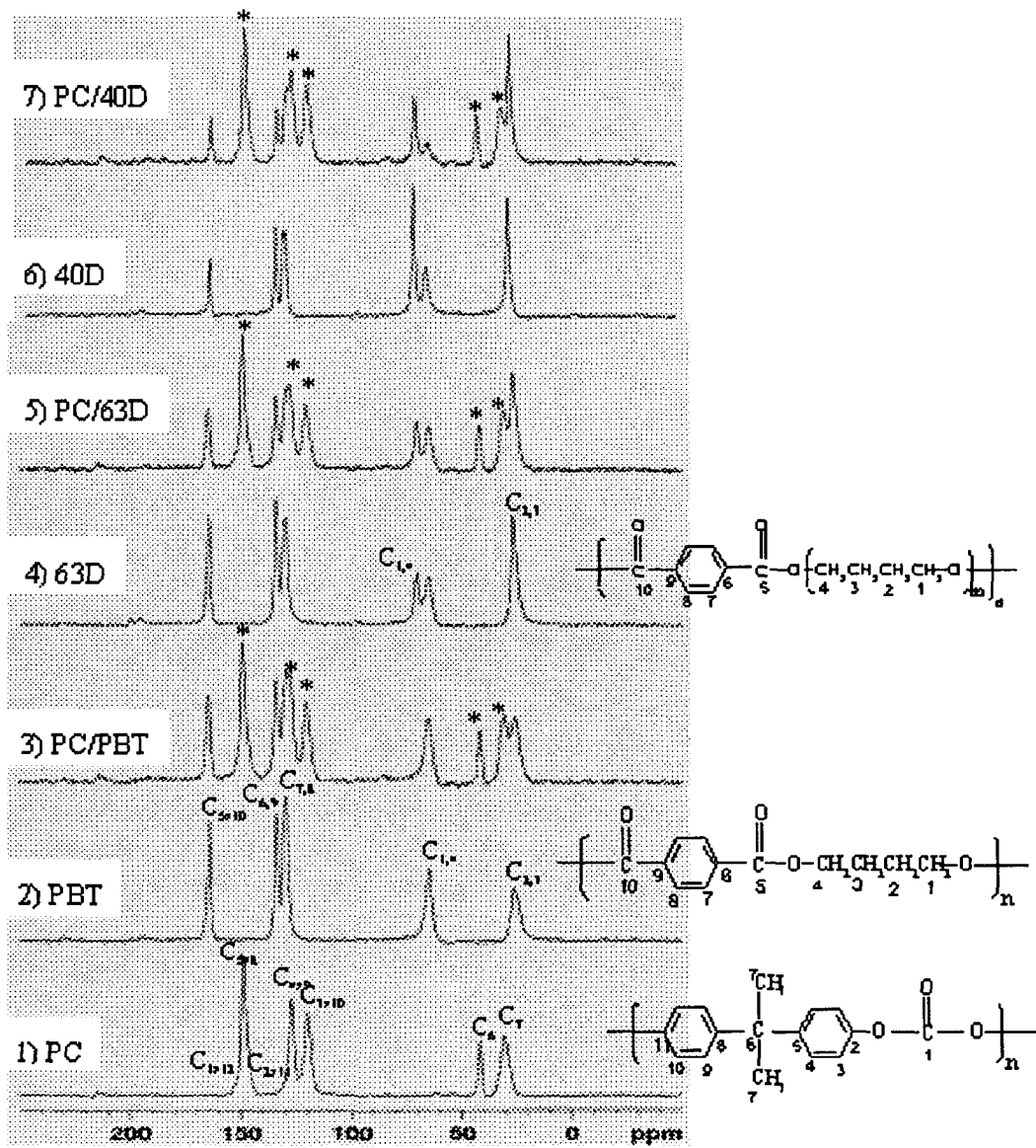
Samples were prepared by KBr pellet and KRS-5 holder method. Spectra were obtained with the FTIR spectrophotometer (BIO-RAD. FTS-60A) using following conditions: Wavenumber; 4000-400 cm<sup>-1</sup>, Resolution number; 4 cm<sup>-1</sup>, Number of scan; 16.

## RESULTS AND DISCUSSIONS

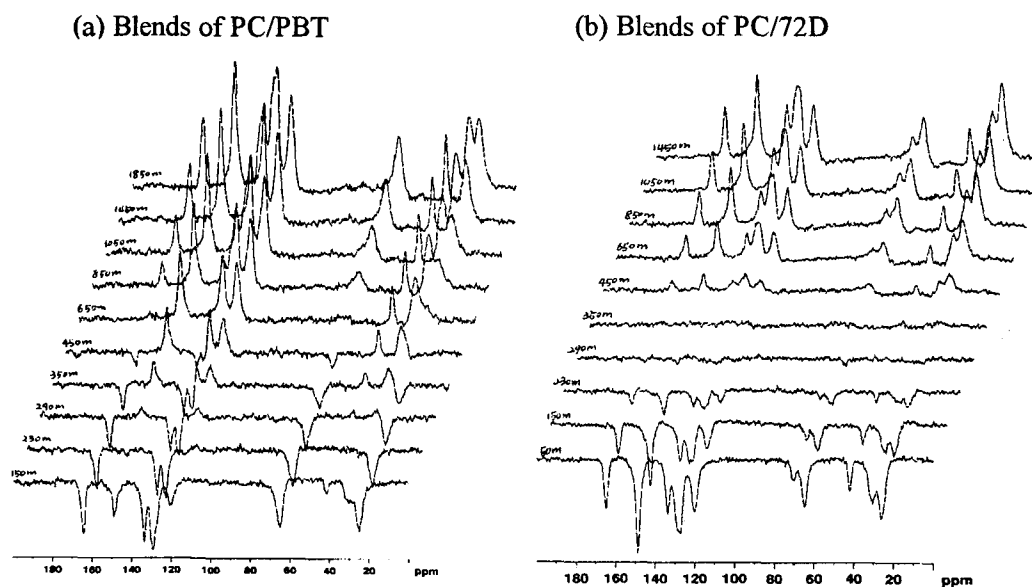
### *Solid-state NMR Spectroscopy:*

All of the carbon resonance was assigned by solid-state NMR and verified by solution-state NMR. And transesterification reaction was examined by <sup>13</sup>C CP/MAS/TOSSDD solid-state NMR spectra of fig. 3.

The chemical shift and/or lineshape could be changed upon blending. Apparent chemical-shift change can be attributed to the modification of both chemical structures like transesterification reaction and polymer conformation during blending. There are no significant chemical shift and lineshape changes. Therefore, no significant transesterification reactions are observed in blends with different compositions of PC/PBT and PC/PEE.



**Fig. 3.**  $^{13}\text{C}$  CP/MAS/TOSSDD Solid-state NMR spectra of 1) PC, 2) PBT, 3) PC/PBT, 4) 63D, 5) PC/63D, 6) 40D, 7) PC/40D. Chemical shift resonances of PC, PBT, PTMEGT is fully assigned. The symbol of \* indicate chemical shift resonances of polycarbonate.



**Fig. 4(a), (b).** inversion recovery  $^{13}\text{C}$  CP/MAS/DD Spectra of PC/PBT(a) and PC/72D(b). The delay time for PC/PBT is 150ms, 230ms, 290ms, 350ms, 450ms, 650ms, 850ms, 1050ms, 1450ms, 1850ms from bottom to top. The delay time for PC/72D is 50ms, 150ms, 230ms, 290ms, 350ms, 450ms, 650ms, 850ms, 1050ms, 1450ms from bottom to top.

Thermal property and morphology upon blending of five different compositions were already studied by DSC, RMS, TEM, and AFM (10). The morphology studied by TEM and AFM indicates PC/PBT blend clearly shows cocontinuous two-phase structure and similar results were obtained in PC/40D blend. However, There are no such phase contrast in PC/70D, PC/63D, and PC/55D. But the results of TEM and AFM micrograph could not explain why these morphology changes with different contents of elastomer happen and how molecular structures change upon blending.

These morphology changes and miscibility in blends are explained by inversion recovery  $^{13}\text{C}$  CP/MAS/DD solid-state NMR experiments. Inversion recovery time  $\tau$  in pulse program of figure 2 is from 30ms to 1850ms. If there is a specific interpolymer interaction between component polymers, molecular motion of the interaction region of the individual polymer in the mixture is expected to be different from that of pure solutions. In our cases, there are no specific interactions like transesterification reaction and each carbon of specific composition of PEE blending has almost the same  $^{13}\text{C}$  spin-lattice relaxation times ( $T_1$ ) after blending. Both  $^{13}\text{C}$ - $T_1$  values for pure polymers and for a mixture with some concentration of PEE are the same. Therefore the effects of blending on molecular motion and miscibility could be explained. In figure 4(a), all carbon resonance of PC are positive in  $\tau = 350\text{ms}$  but all carbon resonance of PBT are positive in  $\tau > 850\text{ms}$ . Therefore the blended PC/PBT is to

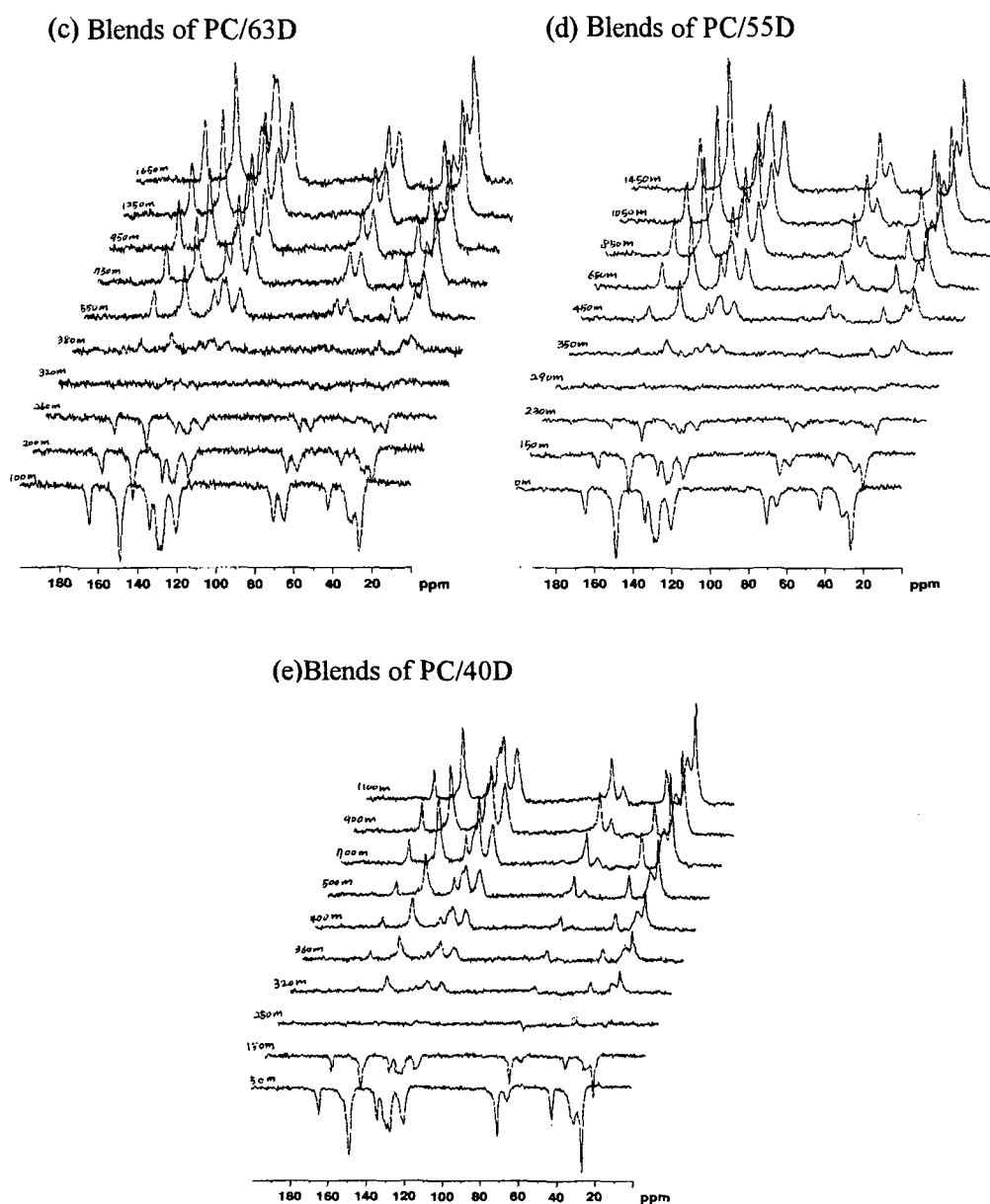


Fig. 4(c), (d), (e). inversion recovery  $^{13}\text{C}$  CP/MAS/DD spectra of PC/63D (c), PC/55D(d) and PC/40D. The delay time for PC/63D is 100ms, 200ms, 260ms, 320ms, 380ms, 550ms, 750ms, 950ms, 1250ms, 1650ms from bottom to top. The delay time for PC/55D is 50ms, 150ms, 230ms, 290ms, 350ms, 450ms, 650ms, 850ms, 1050ms, 1450ms from bottom to top. The delay time for PC/40D is 50ms, 150ms, 250ms, 320ms, 360ms, 400ms, 500ms, 700ms, 900ms, 1100ms from bottom to top.

have two phases of immiscible mixing states. But figure 4(b) is different from figure 4(a). All carbon resonance of PC and 72D has same  $^{13}\text{C}$   $T_1$  values. None of carbon resonance are observed when  $\tau = 350\text{ms}$ . This is the reason why no phase contrast is observed by TEM and AFM before (10). So the blend of PC/72D might have single phase of miscible mixing states. PC/63D and PC/55D shows same behavior like PC/72D even though the time when all carbon resonance are zero are at  $\tau = 320\text{ms}$  and  $290\text{ms}$ . We found out the time when all carbon resonance are zero is decreased when the elastomer content is increased. Therefore the  $^{13}\text{C}$   $T_1$  is shorter and crystalline PBT polymer become amorphous state after blending. The blends of PC/40D are quite different from other blends that have elastomer, PEE. Not all carbon resonance has zero magnetization at the same  $\tau$ . Therefore each carbon has different  $^{13}\text{C}$   $T_1$  and molecular motion is different. So this blends of PC/40D blend will have two different phases of immiscible mixing. Even though PC/PBT in PC/40D might have same  $^{13}\text{C}$   $T_1$  but PEE elastomer has even faster motion, which is different pattern of molecular motion of that of PC/PBT blend.

Therefore, blends of PC/PBT elastomer with 15%(72D) to 42%(55D) of soft segment seem to be single phase miscible mixing but those of PC/PBT and PC/PBT elastomer with 62%(40D) of soft segment are not miscible mixing and show two phases. These results explained why PC/PEE blending with different content of elastomer show different morphology like cocontinuous two phase (PC/PBT), single phase (PC/72D, PC/63D, PC/55D), and two phases again (PC/40D).

Miscibility and exchange reaction could be investigated by  $^{13}\text{C}$  2D rotor-driven spin diffusion experiment. The cross-peak between different species represent spin-diffusion among them. For immiscible blending, only intrapolymer cross-peaks within one polymer are observed. But for miscible blending, interpolymer cross-peaks are observed. Miscibility and the spin-diffusion rate can be deduced from the interpolymer cross-peaks between well-resolved  $^{13}\text{C}$  resonances.

In figure 5(a), PC/PBT seems to be well blended because several intrapolymer cross-peaks are measured all the time and no transesterification reactions are observed. In figure 5(b), we found out interpolymer cross-peaks between PC and 63D as well as intrapolymer cross-peaks to support single phase miscible mixing. The intrapolymer cross-peak of PC/40D in Fig. 5(c) is about same as that of PC/PBT. Therefore, this 2D  $^{13}\text{C}$  rotor driven spin diffusion solid-state NMR spectra also explained that the blends of PC/PBT elastomer with 15% to 42% of soft segment seem to be single phase miscible mixing but those of PC/PBT and PC/PBT elastomer with 62% of soft segment are not miscible mixing shown cocontinuous two phases.

#### ***Solution state NMR spectroscopy and IR Studies:***

$^1\text{H}$  Solution NMR data does not show any evidence for transesterification reaction. Extra peak at 8.06ppm and 8.28ppm will be observed if transesterification reaction of bisphenol A type polycarbonate and polybutylene terephthalate is occurred (6).



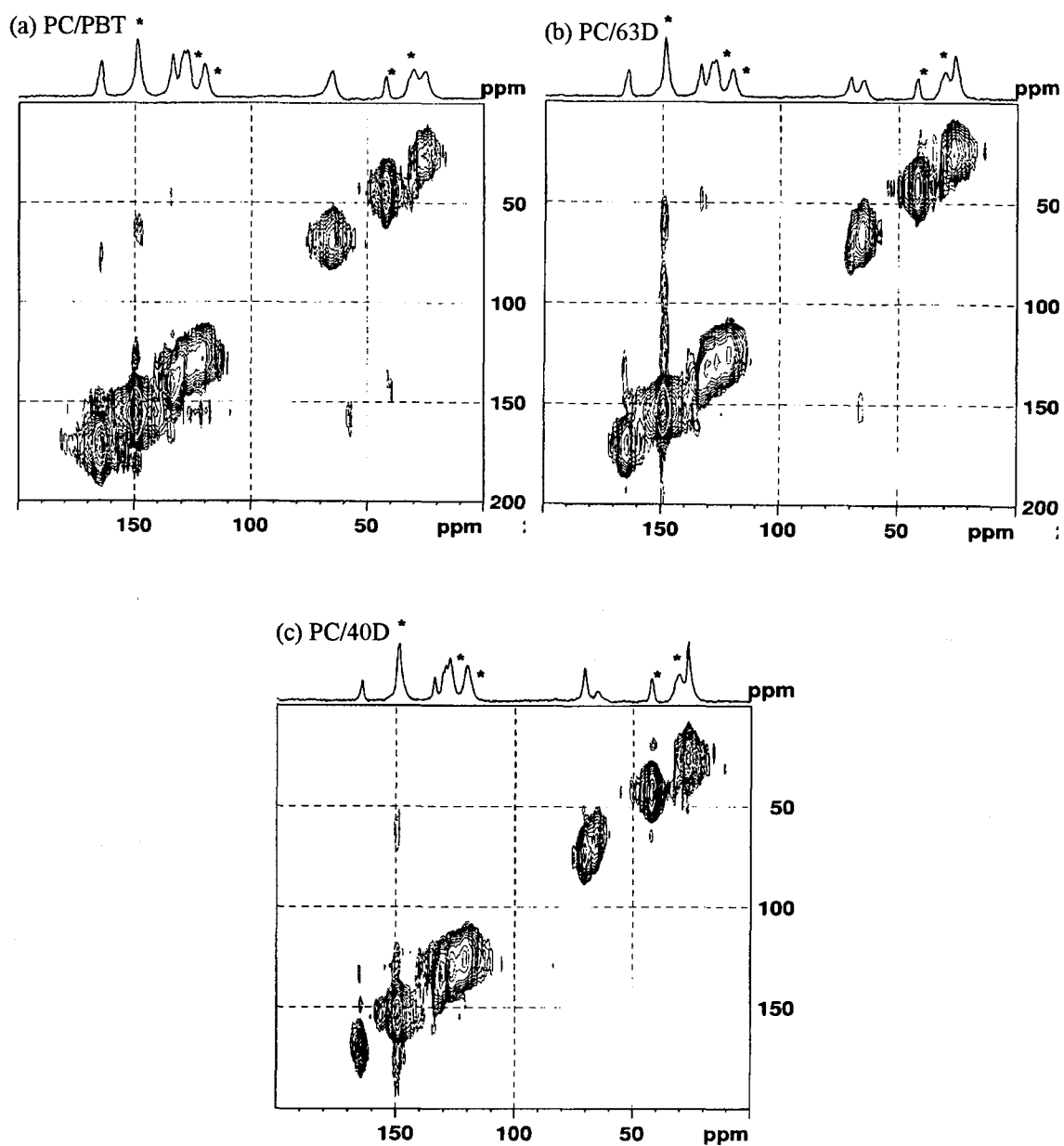


Fig. 5. 2D  $^{13}\text{C}$  rotor driven spin diffusion solid-state NMR spectra of (a) PC/PBT (b) PC/63D (c) PC/40D. The symbol of \* indicate chemical shift resonances of polycarbonate.

IR data also does not show any extra peak at 1740 and 1070 $\text{cm}^{-1}$  which are refer to c=o stretching absorption of different combination.

## CONCLUSIONS

The application of solid-state nuclear magnetic resonance spectroscopy (NMR) to examine the microstructure upon blending is on PC/PBT, PC/72D, PC/63D, PC/55D, and PC/40D. Chemical shift, line shape, relaxation time, and spin diffusion of solid-state NMR technique are quite useful to study polymer blending and provide a molecular interpretation of macroscopic properties of synthetic polymers in bulk.

In this study, miscibility and morphology of blending of bisphenol-A type polycarbonate and poly (ester-ether) elastomer with different compositions are studied by solid-state NMR spectroscopy. The blends of PC/PBT elastomer with 15% to 42% of soft segment seem to be single phase miscible mixing and those of PC/PBT and PC/PBT elastomer with 62% of soft segment are cocontinuous two phase immiscible mixing.

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