

The Interchange Reaction between Poly(ethylene terephthalate) and Poly(*m*-xylylene adipamide)

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ABSTRACT: The interchange reaction in blends of poly(ethylene terephthalate) (PET) and poly(*m*-xylylene adipamide) (MXD6) has been characterized in terms of changes observed in spectra obtained with a 600-MHz ¹H-NMR. The selective degradation of PET components in the blends was carried out in the NMR tubes prior to evaluation. Results indicate that there is no chemical reaction between the PET and MXD6 in the absence of sodium *p*-toluenesulfonate catalyst. The presence of the catalyst activates the interchange

reaction between these two resins. A mathematical method was applied to calculate the degree of randomness of PET-MXD6 copolymer. In addition, the reaction degree was found to be affected by exposure temperature, time, shear rate, and catalyst concentration. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3449–3461, 2009

Key words: poly(ethylene terephthalate); poly(*m*-xylylene adipamide); interchange reaction; selective degradation

INTRODUCTION

One method used to provide materials suitable for specific demands in the polymer industry is to combine the properties of known polymers, rather than to synthesize new ones. In the case of blending two condensation polymers, control of the interfacial tension across the boundaries of the blends plays an important role in determining the desired properties. One of the methods for improving the interfacial tension utilizes an interchange reaction such as transesterification or transamidation. Generally, the interchange reactions take place at elevated temperatures, often in the presence of appropriate catalysts. As a result of the interchange reactions, portions of the blends can be transformed into block copolymers. With increased extent of reaction, their block lengths can decrease with the eventual result of the formation of copolymers with near random distributions of repeat units. Such copolymerized reaction products can significantly improve the compatibility of the blends because portions of copolymer material can provide good adhesion with each of the appropriate PET/MXD6 blend components.

There have been significant numbers of research studies of the interchange reactions that occur

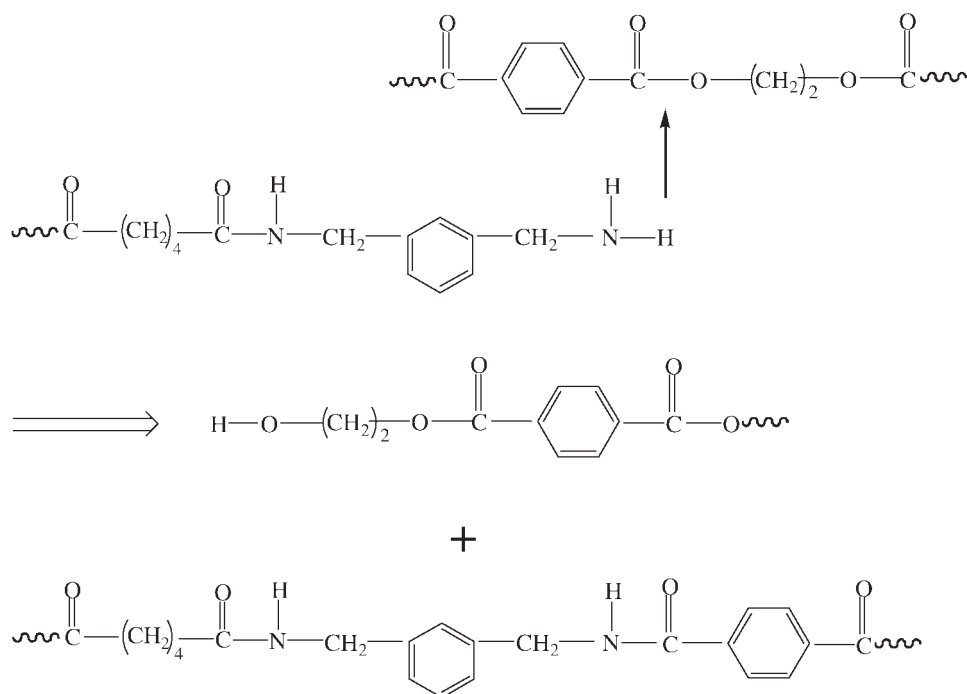
between two polycondensates. These studies include polyester–polyester^{1–13} and polyamide–polyamide^{14–16} systems. Research has also included the interchange reactions between polyesters and some polyamides.^{17–26} Fewer investigations; however, have been performed to elucidate the nature and kinetics of the ester interchange reaction between poly(ethylene terephthalate) (PET) and poly(*m*-xylylene adipamide) (MXD6). This blend has recently attracted technical and commercial interest because the MXD6 component helps to improve the gas barrier properties of containers and other articles made from it. The challenge is to achieve the improved gas barrier, while maintaining good optical clarity through enhancement of the interchange reaction between the PET and MXD6 and thus overcome their incompatible nature. This work was done with the specific objectives of improving their gas barrier properties and optical clarity as well as to elucidate the mechanism of the specific reactions of PET and MXD6 nylon.

EXPERIMENTAL

The PET and MXD6 resins used in this study are commercial polymers that were prepared by melt phase followed by solid state polymerization. The Voridian Aqua WA314 PET, with a number average molecular weight of 25,800 g/mol and intrinsic viscosity of 0.75 dL/g, was used as supplied without further treatment. The Mitsubishi Gas Chemical Company 6007 MXD6 had a number average molecular weight of 25,900 g/mol and a relative viscosity

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Scheme 1 Outer amide-internal carbonyl interchange reaction.

of 2.7 dL/g. It was also used without any additional treatment. Both polymers have FDA approval for container applications suitable for food grade resins; however, no additional specifications are available. The deuterated sulfuric acid (D_2SO_4) and deuterated trifluoroacetic acid (*d*-TFA) NMR solvents were purchased from Cambridge Isotope Laboratory and the sodium *p*-toluenesulfonate catalyst from Sigma Aldrich.

A Hakke Rheomex single screw extruder was used to prepare a master batch of sodium *p*-toluenesulfonate catalyst in PET at a concentration of 5% (wt/wt). This master batch was used in conjunction with the PET and MXD6 materials to prepare the desired blend compositions. Temperatures of extruder zones 1, 2, and 3 were held, respectively, at 280, 270, and 270°C, and the screw speed was maintained at 60 rpm.

A Werner and Pfleiderer (ZSF-30) self-wiping corotating twin-screw extruder was used for all other melt blending operations. With the screw speed at 300 rpm, the temperatures of zones one through five, as well as the exit die, were 270°C and the nitrogen flux was 100 cc/min. Extrudate from the twin strand die was immediately quenched to 15°C in a water trough and pelletized using a Conair (Jetro Division) model 304 pelletizer. The speed of the pelletizer was adjusted to maintain a continuous strand from the die to the pelletizer and obtain pellets at a constant output rate of 12–13 kg/h. The PET/MXD6 blends were all prepared with 90% PET and 10% MXD6, and their catalyst content was varied from 0 to 5% (wt/wt).

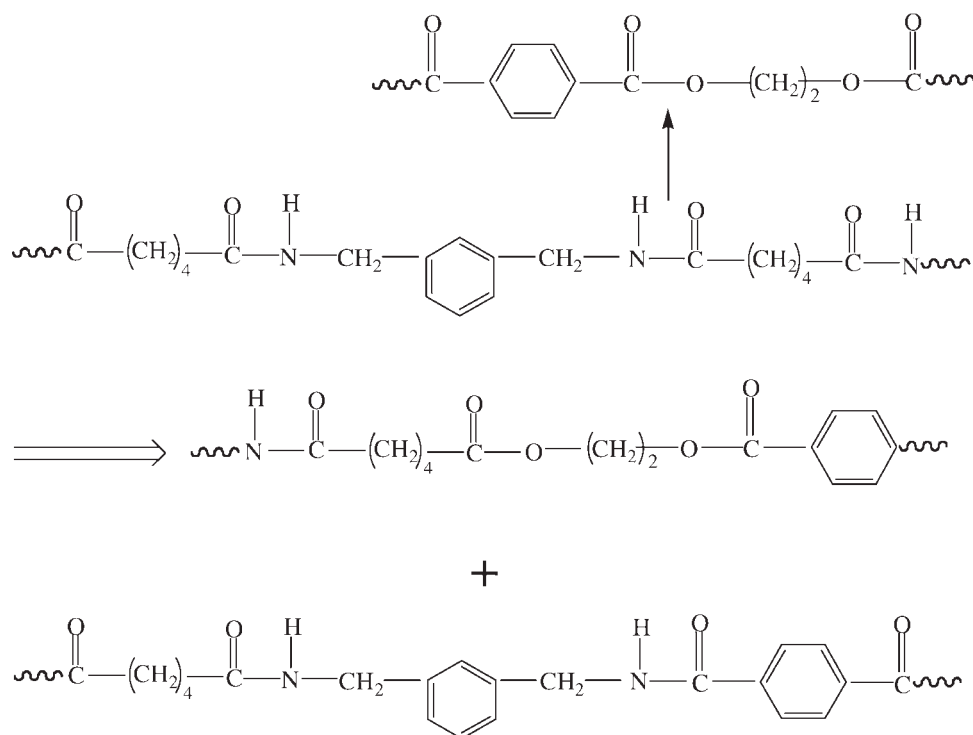
All materials were dried before being blended or processed. PET and MXD6 were dried, to moisture levels of less than 0.005%, in a Conair dehumidifying air dryer at 150°C for 10–12 h. Each pelletized blend material was vacuum dried at 120°C for 12 h before further use.

A Rheometric Scientific RDA III viscoelastic tester, with double parallel plate geometry was used to prepare PET and MXD6 blend samples with specified additional reaction conditions. A nitrogen purge was used to prevent degradation.

NMR experiments were performed in an INOVA-600-MHz NMR instrument. The sample weight was about 5 mg. The acquisition time was 3 s, and the recycle time was 4.73 s. The number of transients was 64, and the temperature was 29°C.

RESULTS AND DISCUSSION

Two possible reaction routes may be followed, when melt blending PET and MXD6 under reaction conditions sufficient to yield ester interchange reactions and thus form copolymers. In the first case, the outer NH_2 terminal chain ends of the MXD6 react with the inner ester linkages of the PET. This route²⁶ has been designated as an outer amide/inner carbonyl interchange reaction as is illustrated in Scheme I. It should be noted that the indicated reactions are not shown stoichiometrically, because the amounts of copolymer are dependent on level of transamidation. The sample will therefore, contain components of



Scheme 2 Inner amide-inner carbonyl interchange reaction.

each of the homopolymers as well as the resultant copolymer.

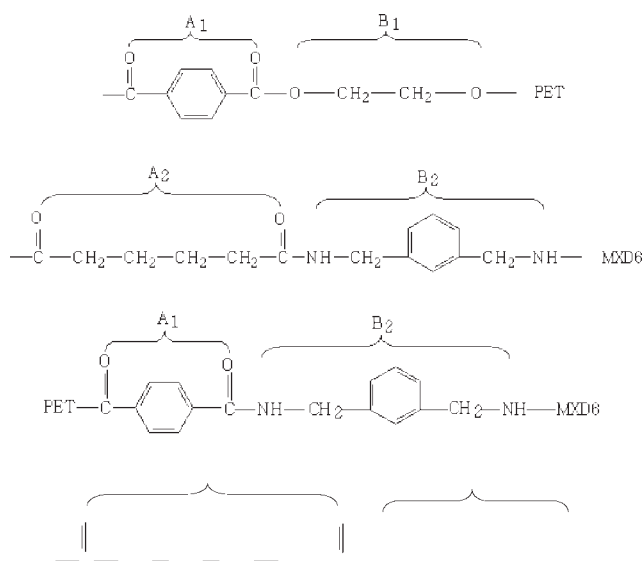
A second reaction scheme²⁶ that has been proposed suggests that the inner amide linkages of the MXD6 can react with inner carbonyl ester linkages of the PET in an inner amide-inner carbonyl interchange reaction as shown in Scheme II.

Following the nomenclature that is commonly recognized when ester-amide interchange reactions occur between a bifunctional polyester A_1B_1 and a bifunctional polyamide A_2B_2 (as in these studies) can lead to the following structural changes given in Scheme III²⁶:

On the basis of work done by Denchev et al.,^{13,26} the use of NMR solvents such as deuterated sulfuric acid (D_2SO_4) will allow determination of the sequence lengths in the reacted (PET/MXD6) blends. For this work; therefore, their recommended procedure has been followed. It utilizes D_2SO_4 to selectively degrade the PET homopolymer and the PET components of the reacted blends, while leaving the sequences of the MXD6 intact. The anticipated degradation of PET with D_2SO_4 yields fragments of degradation products made up of combinations of mono (2-hydroxyethyl) terephthalate (MHET), bis 2-hydroxyethyl terephthalate (BHET), and terephthalic acid (TA). Each of these degradation products can be dissolved in sulfuric acid.

In the following NMR experiments, polymer samples of PET, MXD6, and the various PET/MXD6

blends were dissolved in deuterated sulfuric acid (D_2SO_4), which will generally attack the ester C—O bond of the PET chain. Figure 1 shows the 600 MHz NMR spectra of pure PET in the deuterated sulfuric acid (D_2SO_4) solvent. Because sulfuric acid can degrade PET chains, the solution of PET changes to a solution of its degradation products. There are two groups of peaks located in the spectrum. A series of



Scheme 3 Structural changes expected to result from ester-amide interchange reaction.

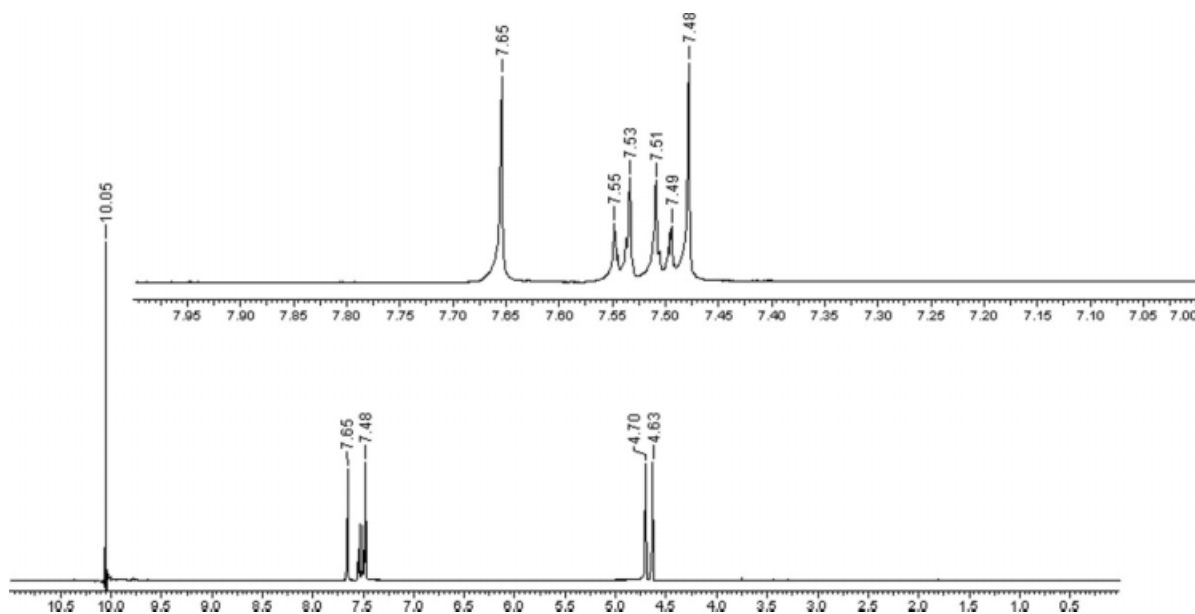


Figure 1 600 MHz ^1H -NMR spectrum of PET.

peaks appears between 7.48 and 7.65 ppm. These peaks belong to the resonance of the benzene ring protons of the degradation products of PET. In the expanded spectrum (aromatic resonance region) of pure PET, $\delta^1 = 7.48$ ppm (singlet) and $\delta^4 = 7.65$ ppm (singlet) belong to bis 2-hydroxyethyl terephthalate (BHET) and terephthalic acid (TA). The doublets δ^2 with $\delta = 7.49$ ppm and $\delta = 7.51$ ppm, and δ^3 with $\delta = 7.53$ ppm and $\delta = 7.55$ ppm are associated with mono (2-hydroxyethyl) terephthalate

(MHET). In the ethylene glycol resonance region, there are two peaks whose positions are $\delta^1 = 4.63$ ppm (singlet) and $\delta^2 = 4.70$ ppm (singlet) and whose intensity ratio is 1 : 1.

Figure 2 displays the 600 MHz NMR spectra of pure MXD6. The chemical shifts of different protons in the MXD6 chain are ^1H (singlet, 0.98 ppm), ^2H (singlet, 1.90 ppm), ^3H (singlet, 3.83 ppm), ^4H (triplet, 6.61, 6.62, and 6.63 ppm), ^5H (doublet, 6.49 and 6.51 ppm), ^6H (singlet, 6.43 ppm). In agreement with

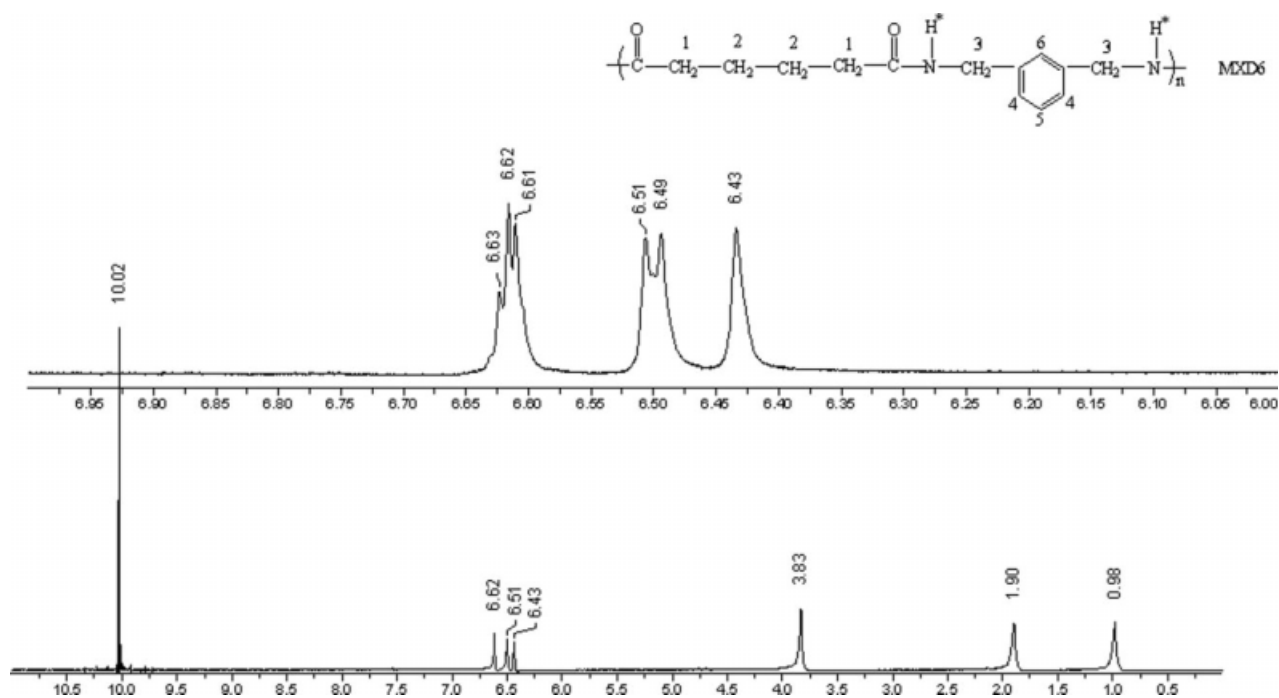


Figure 2 600 MHz ^1H -NMR spectrum of MXD6.

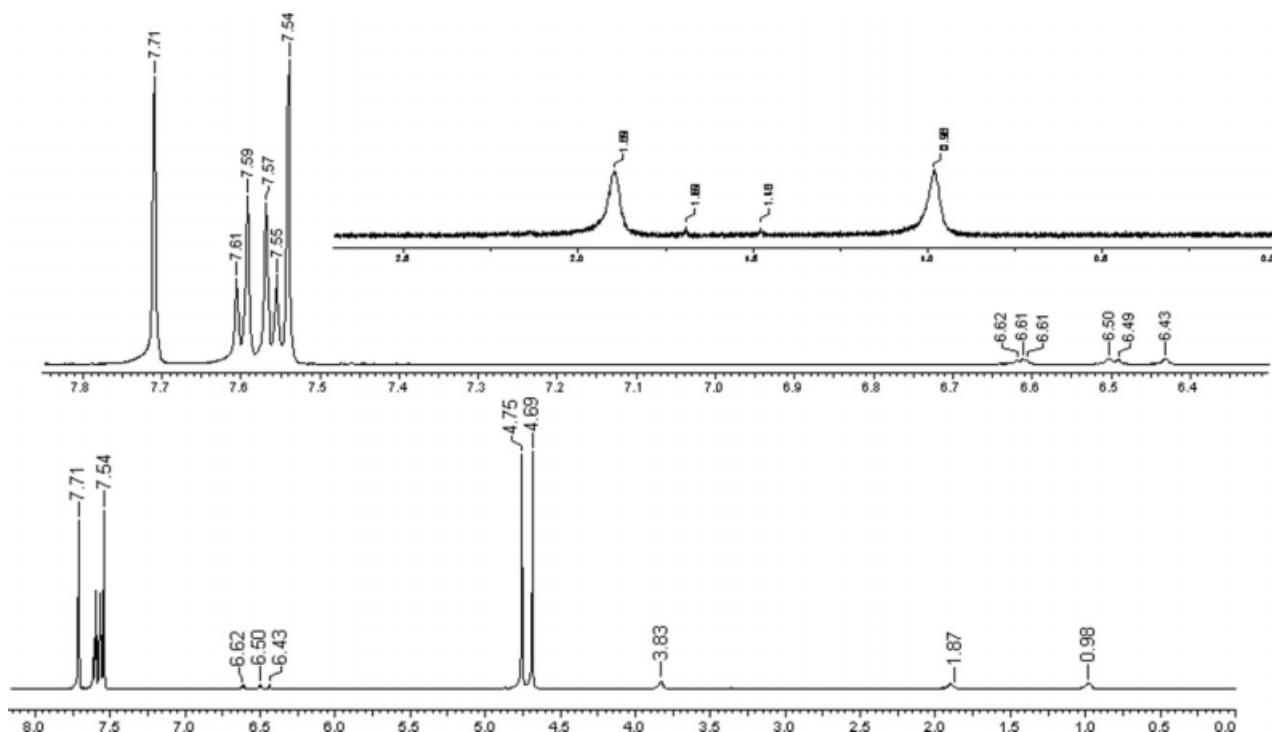


Figure 3 600 MHz ^1H -NMR spectrum of PET/MXD6 (90/10) blend.

Pham et al.²⁴ our data show that the resonance of the amide proton is absent in MXD6 spectra obtained in D_2SO_4 . This is because of the strong H–D exchange of the N–H group with D_2SO_4 as has been established with all types of polyamides. The peaks appearing at $\delta = 6.43$ – 6.62 ppm in Figure 2 belong to the resonance of the benzene ring protons of the MXD6.

Figure 3 gives the NMR spectra of PET/MXD6 (90/10) material melt blended without catalyst. In this figure, there are no new peaks belonging to the PET–MXD6 copolymer. Peaks appearing at $\delta^1 = 0.98$ ppm (singlet), $\delta^2 = 1.87$ ppm (singlet), $\delta^3 = 3.83$ ppm (singlet), $\delta^4 = 6.43$ ppm, 6.50 ppm, 6.62 ppm are attributed to MXD6. Peaks appearing at $\delta = 4.69$ ppm, 4.75 ppm (doublet), and $\delta = 7.54$ – 7.71 ppm belong to PET. The expanded part of the spectrum displays two small peaks which appear at $\delta^1 = 1.48$ ppm and $\delta^2 = 1.69$ ppm. These two peaks are associated with the degradation compounds in the PET resin. From Figure 3, we can conclude that PET did not react with MXD6 and is; therefore, a physical mixture of the two materials.

To facilitate the transamidation reaction between PET and MXD6, sodium *p*-toluenesulfonate catalyst was used. The NMR spectra of the PET/MXD6 blends prepared with 0.5% catalyst are displayed in Figures 4 and 5. While the presence of several new peaks can be observed in these spectra of extruded catalyzed blends, it is important to identify and eliminate peaks associated with the presence of catalyst and degradation residues.

To help clarify the above results and identify the peaks resulting from the catalyst, unblended sodium *p*-toluenesulfonate was dissolved in D_2SO_4 and subjected to NMR analysis. As shown in Figure 6, a peak at $\delta^1 = 1.64$ ppm can be attributed to the resonance of the catalyst's methylene group, while those at $\delta^2 = 6.62$ ppm and $\delta^3 = 6.99$ ppm are both associated with the benzene protons in the catalyst. The distance between these two peaks is 0.37 ppm.

As previously shown in Figure 4, the expanded part of the spectrum displays two new sets of peaks. They appear as a doublet at δ^1 with $\delta = 6.48$ ppm and $\delta = 6.49$ ppm and a second doublet at δ^2 with $\delta = 6.84$ ppm and $\delta = 6.85$ ppm. These two doublets are very clear and the distance between them is 0.36 ppm. These peaks correspond to those of the catalyst, given in Figure 6 at $\delta^2 = 6.62$ ppm and $\delta^3 = 6.99$ ppm and are associated with its benzene ring protons. In Figure 5, the expanded lower chemical shift area of the blend spectrum shows one new peak appearing at $\delta = 1.49$ ppm. This peak corresponds to the catalyst's methylene group at $\delta^1 = 1.64$ ppm, as shown in Figure 6. The peaks appearing at $\delta = 1.40$ ppm and $\delta = 1.61$ ppm result from resonance of the degraded components of the PET materials in the blend.

An NMR spectrum was also obtained for a sample of PET blended with 0.5% catalyst as shown in Figure 7. In addition to the peaks that belong to the pure PET, we see peaks originating from the catalyst at the following positions: $\delta = 1.32$ ppm (singlet), $\delta = 6.30$ ppm, 6.31 ppm (doublet), and $\delta = 6.67$ ppm,

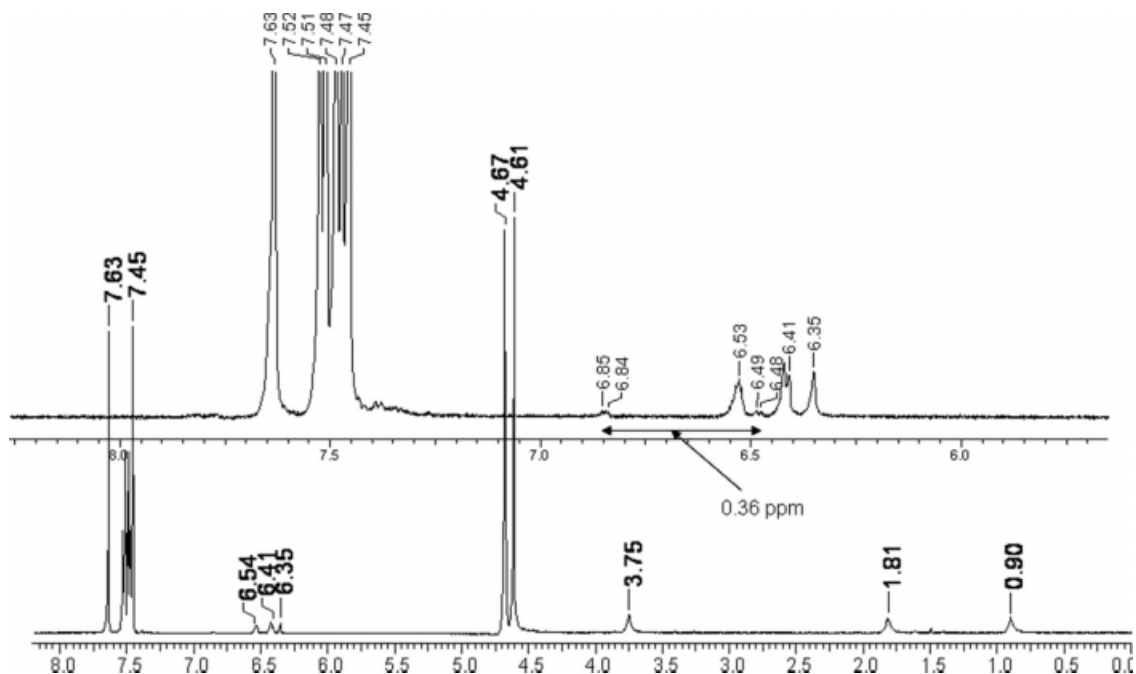


Figure 4 600 MHz ¹H-NMR spectrum of PET/MXD6 (90/10) blend with 0.5% catalyst (part 1).

6.68 ppm (doublet). The distance between the two benzene proton peaks is 0.36 ppm, as was seen in Figures 4 and 6. In contrast, if we examine the spectrum of the uncatalyzed PET/MXD6 blend shown in Figure 3, we find that there are only two small peaks at $\delta = 1.48$ ppm and $\delta = 1.69$ ppm. These peaks are from resonance of the degraded components of the PET materials in the blend and they are between two larger peaks, which belong to the signals of MXD6. We may thus conclude that the new peaks, appearing in Figure 4, are signals of the catalyst in the PET/MXD6 blends rather than those of interchange reaction products of the PET and MXD6.

Examination of the higher chemical shift areas of blend spectra did not reveal any new peaks that could prove an interchange reaction had occurred between PET and MXD6 to form a copolymer. We next considered the lower chemical shift areas of the spectra. The portions of all the spectra, resulting from ethylene glycol segments, were expanded and compared. Examples of these results are given in Figure 8(a,b). As can be seen in Figure 8(a), the extrusion of MXD6 and PET without catalyst does not result in the formation of new peaks in this region. In Figure 8(b), the presence of 0.5% catalyst leads to a very small peak residing on the shoulder

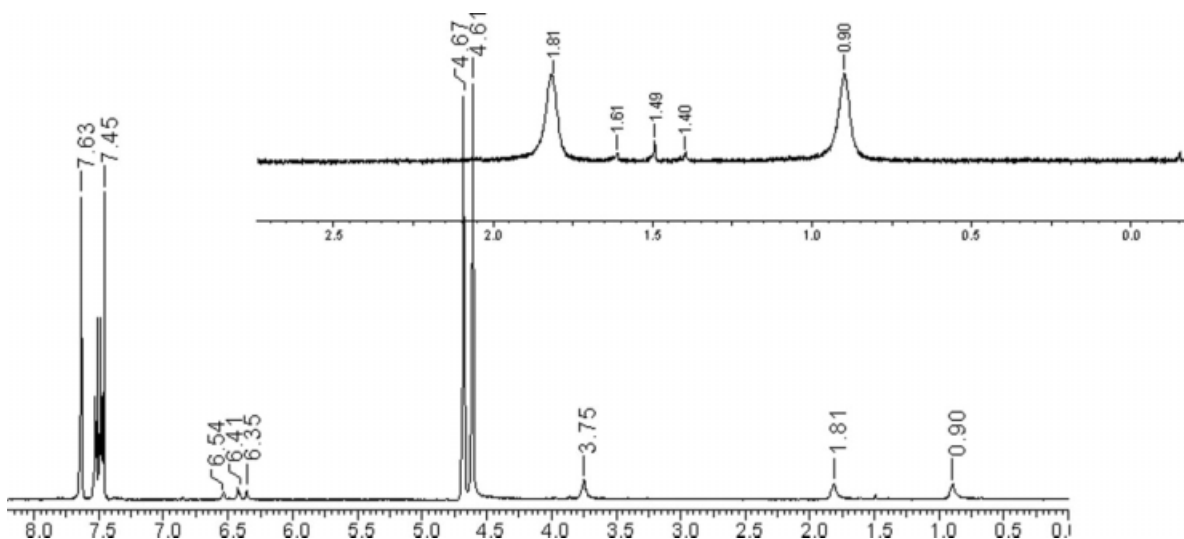


Figure 5 600 MHz ¹H-NMR spectrum of PET/MXD6 (90/10) blend with 0.5% catalyst (part 2).

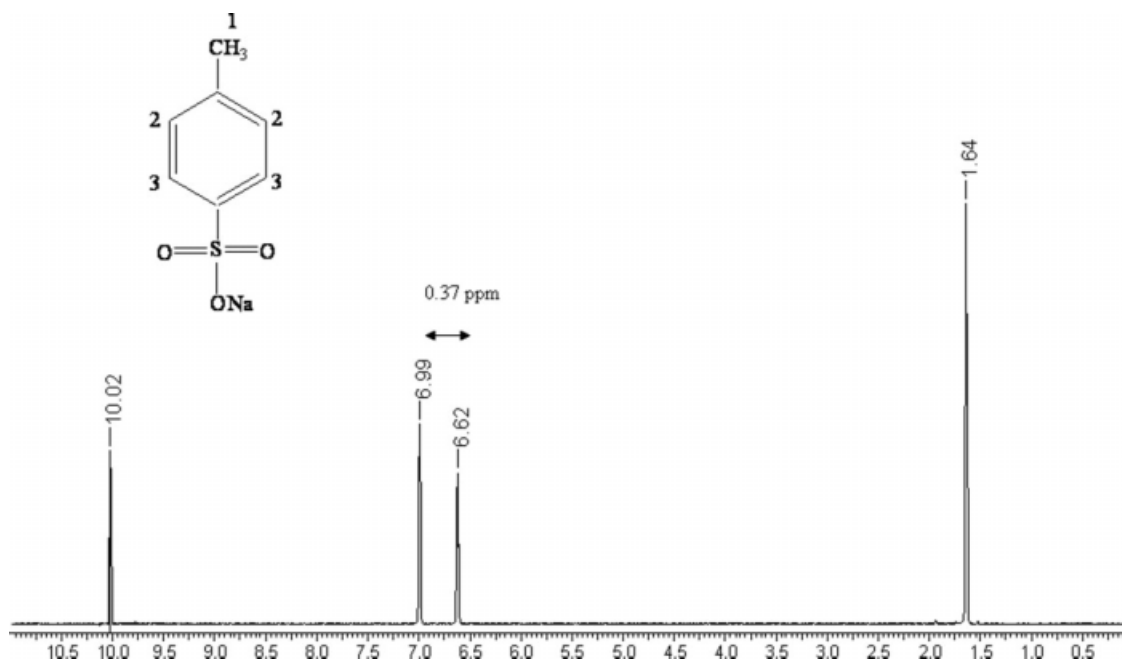


Figure 6 600 MHz $^1\text{H-NMR}$ spectrum of sodium *p*-toluenesulfonate.

of the larger peak resulting from the ethylene glycol segment. To facilitate copolymerization by increasing the reaction time between PET and MXD6 in the presence of the catalyst, a PET/MXD6 (90/10) blend containing 0.5% catalyst was held for 30 min in the RDA III viscoelastic tester at 300°C with a shear rate of 10 s^{-1} . As a result of the increased reaction time, the unclear new peak displayed in Figure 8(b) became larger and better defined as shown in Figure 8(c). This new peak at $\delta = 4.615\text{ ppm}$ cannot be

attributed to the PET, MXD6, or the catalyst. It is the signal of a PET-MXD6 copolymer. In the PET-MXD6 copolymer, the diethylene glycol group should result in two peaks. The observable peak is from the outer CH_2 protons in the diethylene glycol group. The other CH_2 proton is thought to be hidden by the larger peak at 4.67 ppm. When PET, MXD6 and 0.5% catalyst undergo melt mixing in the twin-screw extruder, the reaction time is from 2 to 3 min. This short reaction time leads to a lower reaction degree,

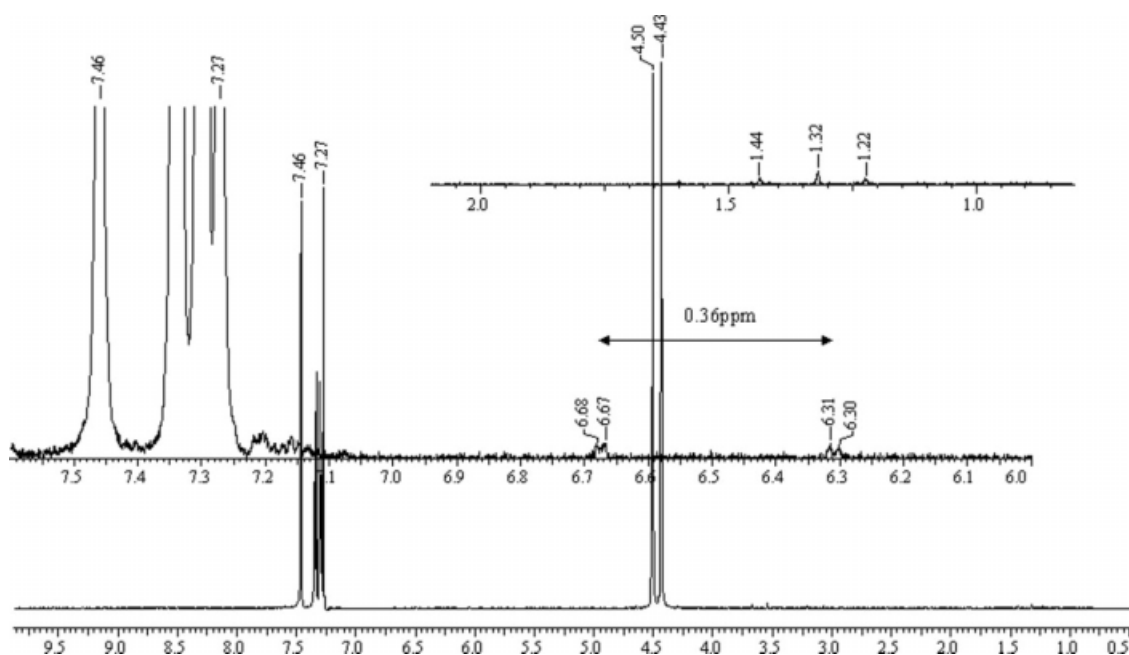


Figure 7 600 MHz $^1\text{H-NMR}$ spectrum of PET with 0.5% catalyst.

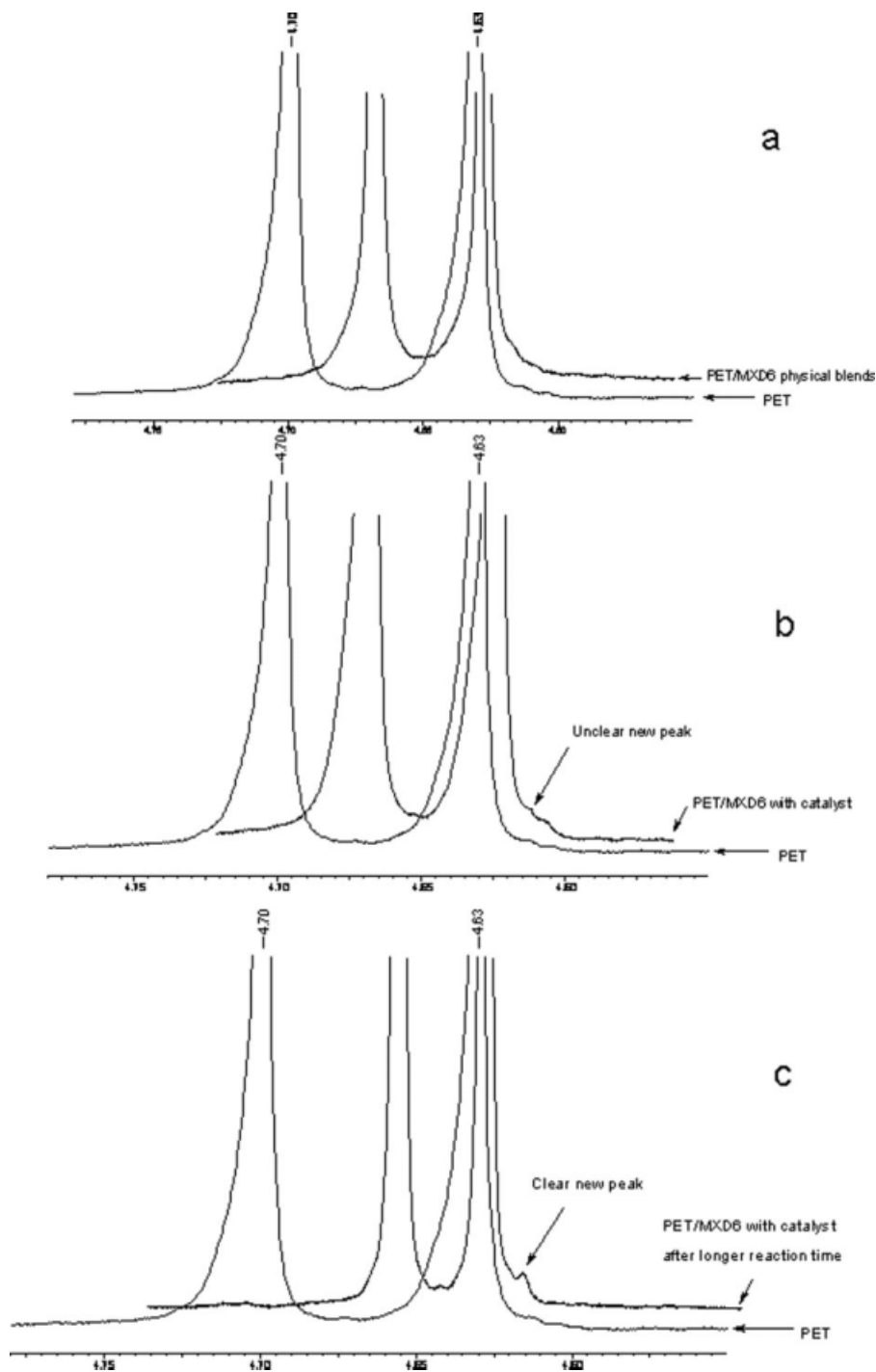
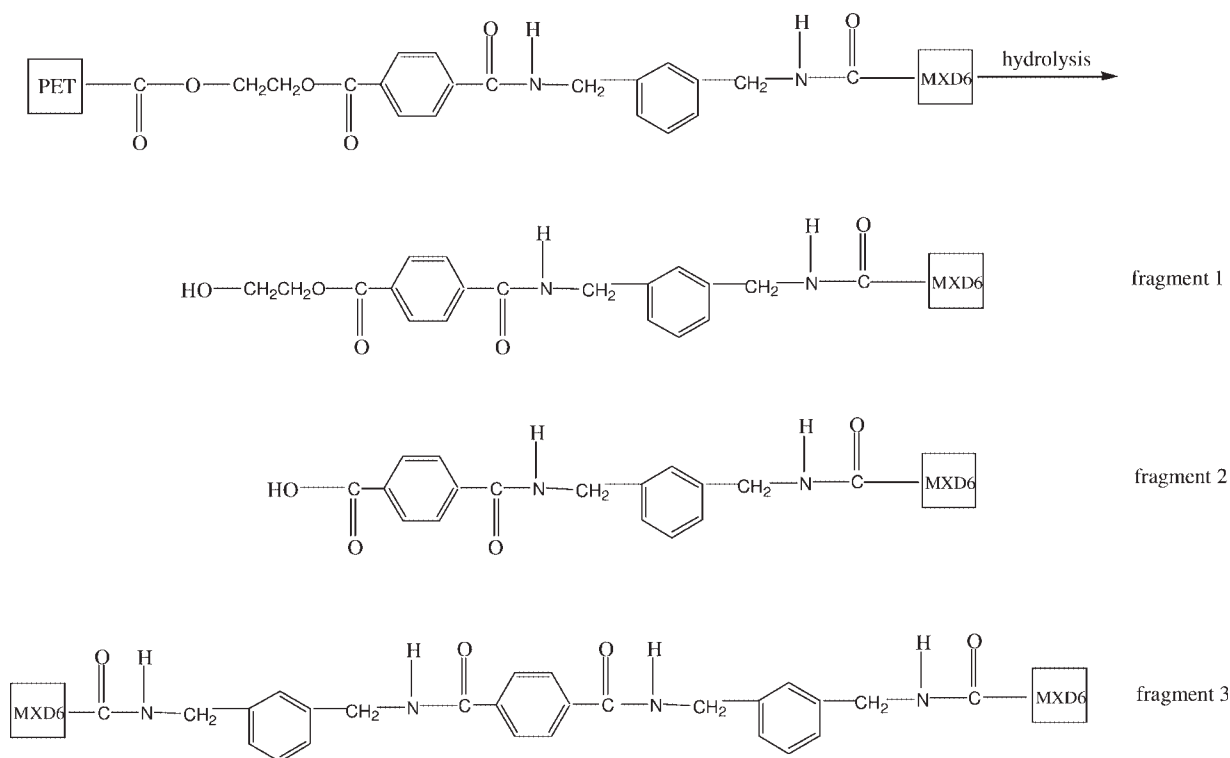


Figure 8 The NMR spectra of the ethylene glycol segment in the pure PET and PET/MXD6 (90/10) blends. (a) no catalyst, (b) 0.5% catalyst, (c) 0.5% catalyst with additional thermal history (longer reaction times) provided by the RDAIII.

and the signal from this small amount of reaction product is unclear in the NMR spectrum. Increased reaction time results in production of higher levels of copolymer and thus provides a more clearly defined NMR signal.

In the previously described NMR experiments, D_2SO_4 is known to degrade not only the pure PET chains but also the PET components in the PET-

MXD6 copolymers. The PET-MXD6 copolymers can have two molecular structures (A_1B_2 and/or A_2B_1), as shown in Scheme III. The new peak appearing in the NMR spectrum is the resonance of the degradation products of the PET component of the PET-MXD6 copolymers. As shown in Figure 8(b,c), the new peak at $\delta = 4.615$ ppm (residing on the shoulder of the ethylene glycol segment peak)

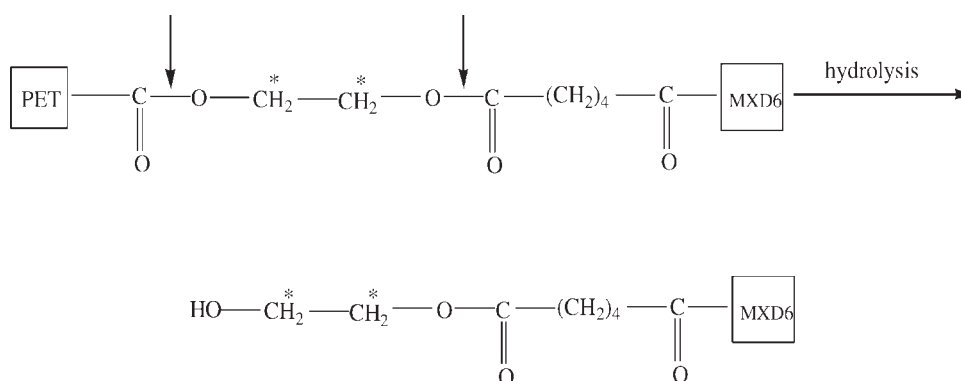


belongs to the resonance of the interchange reaction segment of the PET/MXD6 copolymer and indicates that interchange reactions have occurred between PET and MXD6. The amount of this copolymer is small, thus the peak representing the four protons of the ethylene glycol portion of the copolymer is also small.

Scheme IV shows the most probable fragmentation of the PET-MXD6 transition structure (A_1B_2), after selective hydrolysis of the PET units. The attack by the hydrolyzing agent (D_2SO_4) of the ester C—O group should produce three main fragments (1, 2, and 3), with all of them containing magnetically

unequal protons. Because the level of the interchange reaction between PET and MXD6 is low, the concentration of the interchange reaction products is also low. In the case of an actual NMR experiment, the resonance of these three fragments cannot be seen, because they are overlapped by the resonances of the benzene ring protons of the PET and MXD6 chains.

Scheme V shows the fragmentation mechanism of the PET-MXD6 transition structure (A_2B_1). The new peaks, shown in Figure 8(b,c) with chemical shifts of about $\delta = 4.615$ ppm, are from the ethylene glycol segments in the degradation products. The



replacements of terephthalic acid segments by adipic acid segments give the resonance signals of ethylene glycol protons which are marked by star symbols(*) in Scheme V. These signals are present in the lower chemical shift area, near the ethylene glycol peaks shown in Figure 8(b,c). The relative intensity of the new peak can thus be used to calculate the degree of randomness of the PET-MXD6 copolymer.

We have shown that the interchange reactions between PET and MXD6 can be catalyzed by the sodium *p*-toluenesulfonate. The new peak at $\delta = 4.615$ ppm in the NMR spectra indicates the presence of an ester-amide interchange reaction. For the PET/MXD6 blends with catalyst, the degree of the randomness and the average sequence length of the PET or MXD6 component of the PET-MXD6 copolymer are important. These two factors determine the compatibility of the blends. To establish the effect of the interchange reactions on the microstructure of the copolymer chains, Yamadera and Murano²⁷ have evaluated the average sequence length and the degree of randomness based on the determination of three-component copolycondensates (copolyesters). Following the original work by Yamadera and Murano²⁷ and as shown by Devaux et al.,^{28–32} we have applied their analysis to the current system of PET/MXD6 blends. According to studies by Devaux et al.,^{28–32} analysis of interchange reactions between two dissimilar linear polycondensation polymers yields the following molecular formula.

$$-[(A_1 - B_1)_x - (A_2 - B_1)_y]_m - [(A_1 - B_2)_z - (A_2 - B_2)_w]_n - \quad (1)$$

In this case, A_1 , A_2 , B_1 , and B_2 represent different monomer structural units with the same functionality. Their analyses also yield the average segment lengths of x , y , z , and w . In the case of this study, x represents the PET chain segment length and w the MXD6 chain segment length. The analysis of Deveux et al.^{28–32} leads to the specific segment length of the various components in the reacted blended material, as follows:

$$x = \frac{[A_1B_1]}{[A_1B_2]} + 1 \quad (2)$$

$$y = \frac{[A_1B_2]}{[A_1B_1]} + 1 \quad (3)$$

$$z = \frac{[A_1B_1]}{[A_2B_2]} + 1 \quad (4)$$

$$w = \frac{[A_2B_2]}{[A_2B_1]} + 1 \quad (5)$$

where the degree of randomness (B) of the copolycondensate is given by eq. (6).

$$B = \frac{1}{x} + \frac{1}{w} \quad (6)$$

When B is lower than 1, the block copolymer consists of long segments of each of the two components. If B is 0, there is no copolymer, and the product is a physical mixture of the two components. Values of B greater than 1 indicate the formation of a more random copolymer.

Equations (1)–(6), based on the equal molar ratio of two polycondensates, were introduced by Deveux et al.^{28–32} to calculate the sequence length and the degree of randomness of the copolymer. These equations must be adapted to determine the degree of randomness and average sequence length of the PET-MXD6 copolymer. This is because the PET/MXD6 blends with different contents of MXD6 and catalyst do not have equal molar ratios of PET and MXD6. Equations (1)–(6) have thus been adapted to obtain eqs. (7)–(15) to estimate the results of this work more accurately.

As previously discussed, in the PET-MXD6 copolymer, the diethylene glycol group should be seen as two peaks in the NMR spectrum. The single “new” peak is thought to represent the outer CH₂ protons in the diethylene glycol group, with the other CH₂ proton hidden by the larger peak at 4.67 ppm. The relative intensity of the NMR signal of the new peak is equal to the relative number of the outer CH₂ protons in the diethylene glycol group. The relative intensity of the outer CH₂ protons should also be the same as that of the other CH₂ protons. Two times the relative intensity of the new peak; therefore, can be used to reflect the relative intensity of all four protons, from the ethylene glycol segment of the A_2B_1 copolymer (shown in Scheme III).

$$\text{Molar ratio 1} = \frac{\text{RI}_{4.61-4.67\text{ppm}}}{\text{RI}_{0.90\text{ppm}}} \quad (7)$$

$$\text{Molar ratio 2} = \frac{\text{RI}_{4.61-4.67\text{ppm}}}{\text{RI}_{1.81\text{ppm}}} \quad (8)$$

$$\text{Molar ratio 3} = \frac{\text{RI}_{4.61-4.67\text{ppm}}}{\text{RI}_{3.75\text{ppm}}} \quad (9)$$

$$L_{\text{PET}} = \frac{(\text{RI}_{4.61-4.67\text{ppm}} - \text{RI}_{\text{new peak}}) / \text{mole ratio}}{2 \times \text{RI}_{\text{new peak}}} + 1 \quad (10)$$

$$L_{\text{MXD6}} = \frac{\text{RI}_{6.35-6.54\text{ppm}}}{\text{RI}_{A_2B_1}} + 1 \quad (11)$$

TABLE I
Experimental Parameters for 10%MXD6/PET with 0.5% Catalyst, and with Additional Treatment in the RDA III Viscoelastic Tester

Variable	Shear rate (s ⁻¹)	Temperature (°C)	Reaction time (min)
Shear rate	1	300	30
	5	300	30
	10	300	30
Temperature	10	290	30
	10	300	30
	10	310	30
Reaction time	10	300	10
	10	300	30
	10	300	60

$$RI_{A_1B_2} = RI_{A_2B_1} = 2 \times RI_{\text{new peak}} \quad (12)$$

$$RI_{6.35-6.54 \text{ ppm}} = \frac{RI_{4.61-4.67 \text{ ppm}} - RI_{\text{new peak}}}{\text{mole ratio}} \quad (13)$$

$$L_{\text{MXD6}} = L_{\text{PET}} \quad (14)$$

$$DR = \frac{1}{L_{\text{PET}}} + \frac{1}{L_{\text{MXD6}}} \quad (15)$$

Small shifts of positions are observed for resonance peaks in some NMR spectra, as a result of degradation caused by the D₂SO₄ solvent used. The relative positions, associated intensities, and the assignments of the peaks; however, do not change. In these calculations, the chemical shift of every peak is based on position given in Figure 4. The peaks of PET are taken as $\delta^1 = 4.61$ ppm, 4.67 ppm, $\delta^2 = 7.45$ –7.63 ppm and those of MXD6 as $\delta^1 = 0.90$ ppm (singlet), $\delta^2 = 1.81$ ppm (singlet), $\delta^3 = 3.75$ ppm

(singlet), $\delta^4 = 6.35$ ppm, 6.41 ppm, 6.54 ppm. In Figure 8(b,c), the small new peak at $\delta = 4.615$ ppm is assigned to the PET-MXD6 copolymer.

Equations (7)–(9) show the molar ratios of PET and MXD6, which depend on different resonance peaks of MXD6. $RI_{4.61-4.67 \text{ ppm}}$ is the relative intensity of peaks appearing at $\delta = 4.61$ –4.67 ppm, which is proportional to the mole content of PET component in the blends. $RI_{x.xx \text{ ppm}}$ is the relative intensity of peaks appearing at $\delta = 0.90$ ppm (singlet), 1.81 ppm (singlet), 3.75 ppm (singlet), which is proportional to the mole content of MXD6 component in the blends. The ratio of the two mole contents is the mole ratio of PET and MXD6 in the blends. Now, we get three values of molar ratio of PET and MXD6, and these three values are based on different resonance of peaks from MXD6. In the calculation of average sequence of length of PET and MXD6 segments in PET-MXD6 copolymer, we use the average of these values to reduce the experimental error. The average molar ratio is displayed in eq. (10). From eq. (2), we deduced eq. (10), which reflects the average sequence length of PET segments in the PET-MXD6 copolymer. From eq. (5), we deduced eq. (11), which reflects the average sequence length of the MXD6 segments in the PET-MXD6 copolymer. In the interchange reaction of PET and MXD6, 1 mol of PET segment will be replaced by 1 mol of MXD6 segment. We, therefore, make an assumption that the mole content of PET-MXD6 copolymer (A_1B_2) is equal to the mole content of PET-MXD6 copolymer (A_2B_1). In the NMR experiments, we detect the existence of new peaks, which reflect the interchange reaction in the PET/MXD6 blends. The resonance of the new peak is the resonance of an ethylene glycol segment in the PET-MXD6 copolymer (A_2B_1), then we can get eq. (12). Equation (13) indicates that the

TABLE II
Relative Intensity, Average Sequence Length, and Degree of Randomness Values Obtained as a Result of Various Experimental Conditions

Constant 10%MXD6/ 90%PET blends with:	Variable	Relative intensity of ethylene glycol segment	Relative intensity of new peak as reference	Molar ratio of PET and MXD6 in the blends	Average sequence length of PET	Degree of randomness of PET-MXD6 copolymer
0.5% catalyst vs. shear rate at 300°C, 30 min	1 s ⁻¹	9710.2	100	9.0	6.3	0.32
	5 s ⁻¹	7706.7	100	9.0	5.2	0.38
	10 s ⁻¹	3250.7	100	8.9	2.8	0.72
0.5% catalyst vs. reaction temperature at a shear rate of 10 s ⁻¹ , 30 min	290°C	4041.1	100	8.9	3.2	0.62
	300°C	3250.7	100	8.9	2.8	0.72
	310°C	618.5	100	9.1	1.3	1.56
0.5% catalyst vs. reaction time at a shear rate of 10 s ⁻¹ , 300°C	10 min	6275.4	100	9.0	4.4	0.45
	30 min	3250.7	100	8.9	2.8	0.72
	60 min	2986.7	100	8.9	2.6	0.76
Different catalyst content, twin screw extruder only, 300°C	1%	7612.4	100	8.9	5.2	0.38
	2%	6416.9	100	9.2	4.4	0.45
	5%	5652.2	100	8.8	4.1	0.48

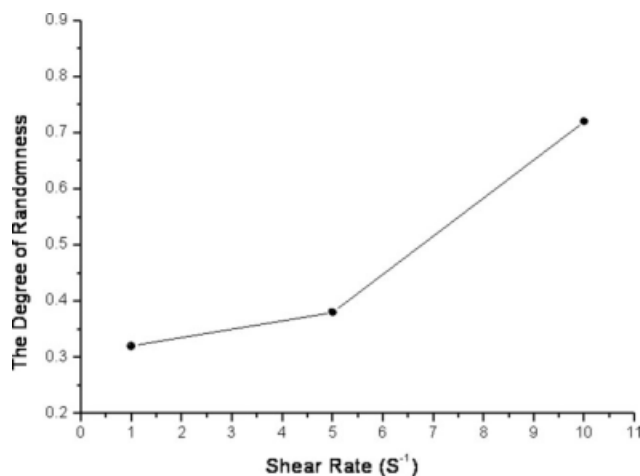


Figure 9 Degree of randomness of PET/MXD6 (90/10) blends with 0.5% catalyst as a function of shear rate at 300°C, 30 min.

molar ratio of PET and MXD6 blends can also be reflected by the ratio of the relative intensity of ethylene glycol segment from PET and the relative intensity of benzene protons from MXD6. From eqs. (10)–(13), we can get eq. (14), which means that the average sequence length of PET (L_{PET}) is equal to the average sequence length of MXD6 (L_{MXD6}). Equation (15) can be used to calculate the degree of randomness of PET-MXD6 copolymer and eq. (15) is deduced from eq. (6). Equations (10)–(15) are the basic equations used to calculate the degree of randomness of PET-MXD6 copolymer.

As previously described PET/MXD6 blends with 0.5% catalyst were melt-mixed in the twin-screw extruder, in which the shorter reaction times led to the lower reaction degree. In these cases, the relative intensity of the NMR new peak shown in Figure 8(b)

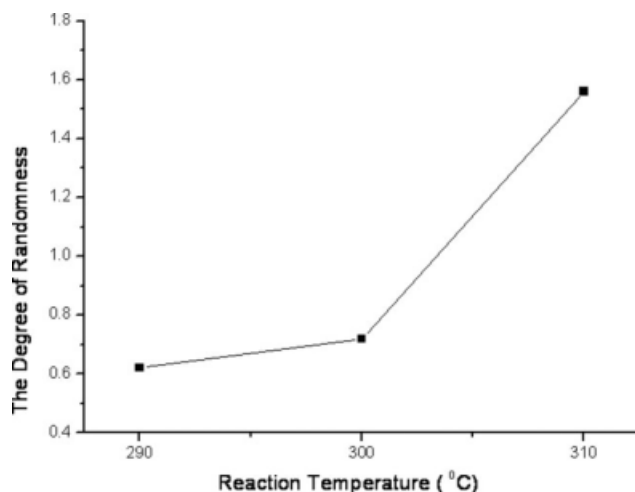


Figure 10 Degree of randomness of PET/MXD6 (90/10) blends with 0.5% catalyst as a function of reaction temperature at a shear rate of 10 s^{-1} , 30 min.

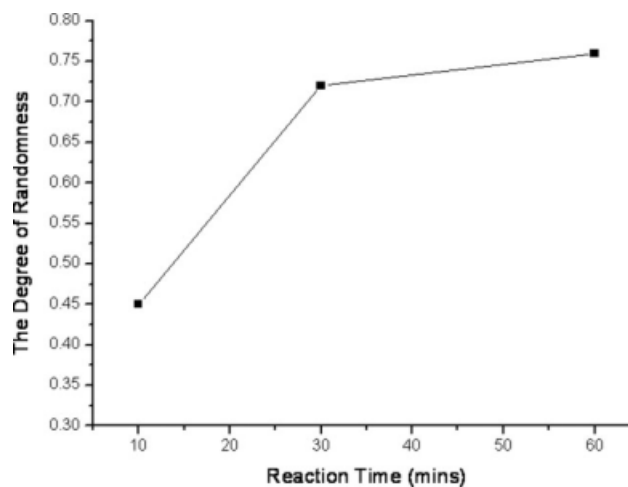


Figure 11 Degree of randomness of PET/MXD6 (90/10) blends with 0.5% catalyst as a function of reaction time at a shear rate of 10 s^{-1} , 300°C.

is very small, and the calculation of the degree of randomness is difficult. After additional blending in the RDA III, to increase the reaction time, the relative intensity of the new peak becomes bigger. This makes the calculation possible. Table I lists the experimental parameters used in the melt-mixed procedure. From the raw data of NMR, we can calculate the degree of randomness of the PET-MXD6 copolymer (after exposure to different temperatures, shear rates, and reaction times) by using eqs. (10), (14), and (15).

Calculated values for average sequence length and degree of randomness, resulting from various experimental conditions are shown in Table II. In Figures 9–12, it can be seen that the degree of randomness of PET/MXD6 blends, with 0.5% catalyst, increases with the increase of the mixing shear rate,

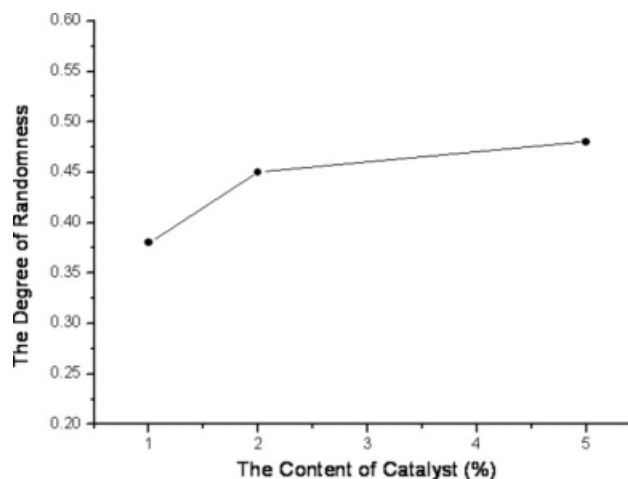


Figure 12 Degree of randomness of PET/MXD6 (90/10) blends (prepared at extrusion temperatures of 300°C) as a function of different content of catalyst.

processing temperature, and reaction time. Of these three factors, the reaction temperature is the most important parameter. For example, in Figure 12, the degree of randomness achieves almost 120% at 310°C. To improve the degree of randomness of PET-MXD6 copolymer, we should process the blends at conditions of higher temperatures, shear rates, and for longer reaction times. Under such processing condition, however, degradation of the blends will probably occur. To improve the degree of randomness of PET-MXD6 copolymer in accordance with lower degradation of the blends, we have increased the catalyst content in the blends. Figure 12 shows that with increased content of the catalyst, the degree of randomness of PET-MXD6 copolymer also increases. The increase of the processing temperature, mixing time and shear rate does improve the reaction degree between two polymers, but it also leads to degradation of the MXD6. The color of the blends becomes somewhat more yellow with the increase of the processing temperature, mixing time and shear rate. A better method to improve the compatibility between PET and MXD6 is by the addition of catalyst at higher concentrations.

CONCLUSIONS

The interchange reaction between PET and MXD6 has been discussed. Various parameters that could influence the interchange reaction have also been included. We obtain the following conclusions.

1. PET and MXD6 do not react with each other without the help of the catalyst.
2. In the presence of the catalyst, the reaction degree between PET and MXD6 can be improved by increasing the reaction time, shear rate, and temperature. These changes can also lead to degradation of the blends.
3. Increasing catalyst content leads to an increased degree of randomness value for the copolymer. In the case of considering the thermal stability of PET/MXD6 blends, one of the more efficient methods that can be used to compatibilize the PET/MXD6 blends is by adding higher concentrations of catalyst.

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