

Polyester 의 개질에 관한 연구

1. NMR에 의한 Copolyester의 분석

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Copolyester Studies

1. Quantitative Analysis of Copolyesters by Nuclear Magnetic Resonance Spectroscopy

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요약 : 핵자기 공명분광법(NMR)을 이용하여 copolyester중의 propylene glycol과 polyethylene glycol등 diol unit의 함량을 조사하였다. Copolyester의 조성은 NMR spectra에 나타나는 특성 group의 proton에 의한 공명 peak의 면적을 비교하여 정량하였다. Dimethyl terephthalate(DMT)와 ethylene glycol (EG) 및 propylene glycol (PG)로 합성된 copolyester는 phenylene proton과 methyl proton에 의해 분석하였고, DMT와 EG 및 polyethylene glycol-400 (PEG-400)으로 합성된 copolyester는 ether 결합에 이웃한 methylene proton과 ester 결합에 이웃한 methylene proton의 chemical shift가 서로 다른 것을 이용하여 분석하였다. 이 결과를 확인하기 위해 gas chromatography를 이용하여 분석한 결과와 비교하였다.

ABSTRACT: A NMR spectroscopic method was used for the determination of the diol contents such as propylene glycol and polyethylene glycol in copolyesters. The quantitative analysis of copolyester compositions was made by comparing the areas of the resonance peaks of the characteristic groups in the spectra. The compositions of the copolyesters made from dimethyl terephthalate with ethylene glycol and propylene glycol, containing whole range of propylene glycol, were determined from the ratios of phenylene vs. methyl protons. The compositions of the copolyesters made from dimethyl terephthalate with ethylene glycol and polyethylene glycol-400, containing less than 30 mole % of polyethylene glycol-400, could be determined from the differences in chemical shifts of ether- and ester-linked methylene

protons of the diols. In order to confirm these results, the gas chromatographic method was used. The result stherefrom correspond to those proposed by NMR method.

INTRODUCTION

In studying copolyesters, it is important to determine the relationship between the compositions and chain structures, and the properties of the copolyesters. Hence the determination of the compositions of copolyesters has received the attentions of many investigators.

The previous analytical methods, commonly used to analyze copolyesters, required the use of gas chromatography, infrared spectroscopy, and wet chemical analysis. Although these methods could be used for the determination of acid and glycol units in copolyesters, they required the degradation step or laborious and troublesome pre-treatment from which good quantitative results might be difficult to be obtained.

However, the nuclear magnetic resonance (NMR) spectroscopic method is more accurate and more rapid than the other methods, since neither the degradation step nor the pre-treatment of the polymer is necessary to obtain the spectra.

Since Percival and Stevence¹ first reported on the use of NMR for the analyses of polyester resins in 1964, owing to its benefits above mentioned, many papers have appeared describing qualitative identification and quantitative determination of unknown copolyesters.²⁻⁹

Recently, NMR spectroscopic method is widely used for the determination of the compositions of copolyesters with rapidity and with fair degree of accuracy.

In this paper, we report a straightforward and accurate method for the determination of glycol contents in ethylene glycol-propylene

glycol-terephthalate copolyester [PET/PT] and in ethylene glycol-polyethylene glycol-400-terephthalate copolyester [PET/(PEG-400)T] systems.

EXPERIMENTAL

Materials:

Practical grade dimethyl terephthalate(DMT) from Mitsui Petrochemical Ind., Ltd., was purified by recrystallization in absolute ethanol twice and dried in vacuum. The melting point was 143°C. Ethylene glycol(EG) and propylene glycol(PG) from Waco Pure Chemical Ind., Ltd., were purified by adding sodium metal, 1g/100ml, and by refluxing under nitrogen for 1 hour, followed by distillation. The boiling points of EG and PG were 55°C and 47°C, respectively, at 1.0 torr. Sodium acetate, calcium acetate, and antimony trioxide from Waco Pure Chemical Ind., Ltd., used as catalysts for the polycondensation reaction, and trifluoroacetic acid from Merck AG, used as NMR solvent, and other reagents were used without further purification.

Copolycondensation:

The copolyesters were prepared by ordinary polycondensation procedure under the reduced pressure.¹⁰ Two types of copolyesters were prepared; the copolyester from DMT with EG and PG, and the copolyester from DMT with EG and polyethylene glycol-400(PEG-400). Each homopolymer was prepared also. The prepared copolyesters were purified by reprecipitation, and dried in vacuum. The reduced viscosities of the copolyesters in the mixed solvent, phenol/tetrachloroethane (60/40 by weight) at 30

°C, ranged 0.58 to 0.70 dl/g.

NMR measurement:

The proton NMR spectra were obtained from the 10% (w/v) solutions of the copolyesters in trifluoroacetic acid at room temperature on Jeol-JNM-MH-100 NMR spectrometer. Tetramethyl silane was used as an internal standard. The relative intensities of the resonance peaks were determined by an electronic integration device attached to the spectrometer. The average of the three integrations of the signal intensities was used to determine the glycol contents in the copolyesters.

Gas chromatographic analysis:

2.00 grams of PET/PT copolyester powder (20 mesh) were stirred in 100 ml of 7.5N methanolic KOH for 1 hour under reflux. Rinsed the condenser with several milliliters of methanol so that the methanol might pass into the sample solution. Added 4N methanolic HCl into the mixture to make the mixture neutral, confirming by pH paper. Filtered the mixture and injected 1 μ l of the clear liquid into the gas chromatography.

A Yanaco Gas Chromatography, Model G-80, with hydrogen flame ionization detector and 9 ft \times 1/4 inch glass column of uncoated Chromosorb 101 60/80, was employed for the analysis with the following operating condition; injection port, 230°C; detector, 230°C; column, isot-

hermal at 190°C; carrier gas and flow rate, helium at 30ml/min. The integrator was a Shimadzu Integrator ITG-4A.

The compositions of the copolyesters were determined by comparing with the standard calibration curve which was obtained by analyzing weighed mixtures of EG and PG in methanol solution for the desired range.

RESULTS and DISCUSSION

1. Copolyesters of dimethyl terephthalate with ethylene glycol and propylene glycol.

The previous methods commonly used to analyze copolyesters required the use of gas chromatography or the wet chemical analysis. Although these methods could be used for the quantitative determination of copolyesters, they might be troublesome, and good quantitative results might be difficult to be obtained. However, the NMR spectroscopic method is more accurate and more rapid than the other methods.

Hence, for the analysis of PET/PT, NMR method is studied and the results therefrom are confirmed by the gas chromatographic method.

1-1. NMR analysis.

The chemical structure of the PET/PT is shown in Fig. 1., where α is the mole fraction of ethylene terephthalate(ET) units of the co-

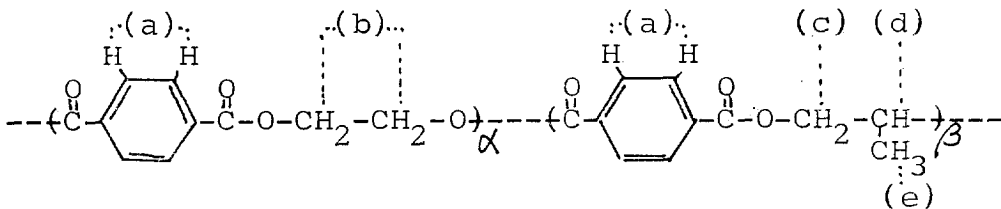


Figure 1. Structure of Copolyester of Dimethyl Terephthalate with Ethylene Glycol and Propylene Glycol.

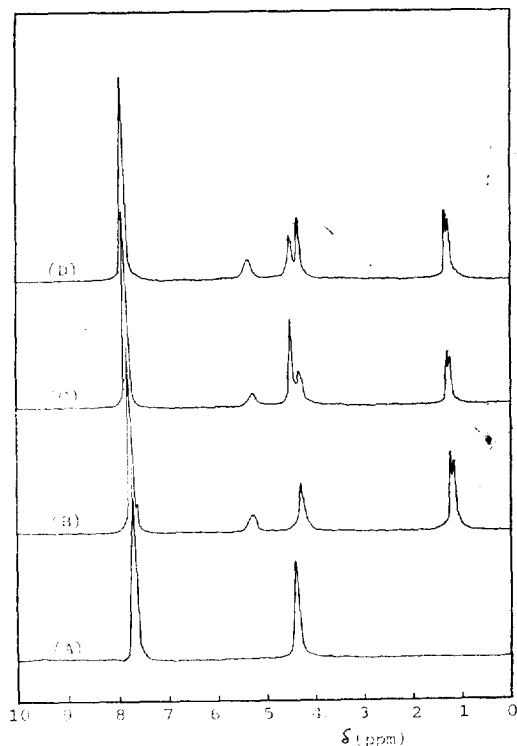


Figure 2. NMR Spectra of Homo- and Copolyesters (A) PET, (B) PPT, (C) PET/PT (47.5/52.5), and (D) PET/PT (12.9/87.1) in Trifluoroacetic Acid (0.1g/ml) at Room Temperature.

polyester and β is that of the propylene terephthalate (PT) units.

In case of polyethylene terephthalate (PET), there are two kinds of protons with different magnetic environments; (a) phenylene protons, and (b) protons of methylene group adjacent to the ester group. For the polypropylene terephthalate (PPT), there are four kinds of protons; (a) phenylene protons, (c) methylene protons, (d) methine protons, and (e) methyl protons. For the PET/PT, there are five kinds of protons, thus five kinds of the corresponding resonance peaks are expected to be appeared in the spectrum of PET/PT copolyester.

Fig. 2. shows the spectra of PET, PPT, and

PET/PT. In case of PET, as shown in Fig. 2-(A), phenylene peak (a) occurs at 7.6 ppm as a sharp singlet and methylene peak (b) occurs at 4.5 ppm. For PPT, phenylene peak (a) occurs at 7.6 ppm, methylene peak (c) at 4.2 ppm, methine peak (d) at 5.2 ppm, and methyl peak (e) occurs at 1.0-1.1 ppm as a doublet because of its vicinity of the methine group. In case of PET/PT, five kinds of peaks occur at the corresponding positions including the two different methylene peaks, (b) and (c).

To support these assignments, the copolyester samples having different compositions are characterized. As shown in Fig. 2-(C), (D), the intensity of methylene peak (c) at 4.2 ppm increases as the amount of PT units in the copolyester increases.

This assignment may be also estimated from the stronger (+)I inductive effects exercised by the $-\text{CH}(\text{CH}_3)-$ group than those by the $-\text{CH}_2-$ group on their neighbouring methylene protons.

In the spectra of PET/PT, the observed chemical shifts are very similar to the results of Birley et al.,^{11,12} who studied the prepolymer made from DMT and PG, and to the results of Murano⁷⁾ on the model compound study of PPT.

In Fig. 2., for the PET, the integrated trace of the phenylene proton peak at 7.6 ppm is almost equal to the integrated trace of the methylene peak (b) at 4.5 ppm. For the PPT, the integrated trace of the methine peak (d) at 5.2 ppm is 1/2 of that of the methylene peak (c), 1/3 of that of the methyl peak (e), and 1/4 of that of the phenylene peak (a). These results coincide with the ratios of the number of the protons in each group and are the basis for calculating the composition of the copolyester.

Thus the composition of the copolyester can be obtained from the ratio of the peak area of

Table I. Composition of PET/PT by NMR Analysis.

Copolyester Sample	A _a (arb. unit)	A _b (arb. unit)	Mole % of PT unit*
EP-1	293.4	11.0	5.0
EP-2	263.5	28.1	14.2
EP-3	262.3	28.1	17.6
EP-4	270.8	42.3	20.8
EP-5	225.1	54.6	32.3
EP-6	198.7	78.2	52.5
EP-7	180.3	99.1	73.3
EP-8	178.6	116.7	87.1

A_a; Area of the phenylene proton peak at 7.6 ppm.

A_b; Area of the methyl proton peak at 1.0 ppm-PT unit; propylene terephthalate unit

*; Determined by the equation(1).

(a) to that of (e), or from the ratio of the peak area of (a) to that of (d), or from the ratio of the peak area of (a) to that of (b) or (c), or from the ratio of the peak area of (b) to that of (c). Having more protons than the methine and methylene groups, and having no interference like the two methylene groups (b) and (c), the methyl proton peak can be integrated more accurately.

To determine the composition of the copolyester, therefore, the ratio of the peak area of the phenylene proton to that of the methyl proton gives a powerful way. This ratio is related to the theoretical phenylene protons vs. the methyl protons ratio, which is given by $4/3\beta$, where β is the mole fraction of PT units in the copolyester, and 4 and 3 correspond to the number of protons in the phenylene and the methyl group, respectively.

On these bases, the integrated areas of those peaks follow the equation;

$$\frac{A_a}{A_b} = \frac{4(\alpha + \beta)}{3\beta} = \frac{4}{3\beta} \dots\dots\dots(1)$$

where, A_a and A_b are the areas of the phenylene and methyl proton resonance peaks, respectively. Hence, β can be calculated from the equation (1) with the obtained values A_a and A_b.

The composition data obtained from the equation (1) by NMR are shown in Table I.

1-2. Gas chromatography.

In order to confirm the results from the NMR analysis, gas chromatographic analysis of the copolyester was carried out.

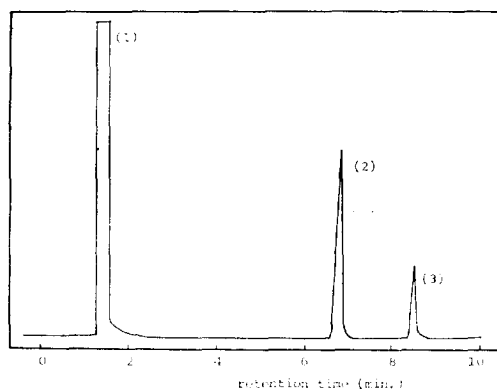


Figure 3. Typical Gas Chromatogram of Ethylene Glycol and Propylene Glycol in Methanol Resulting from PET/PT(79.9/20.1) Peak Assignments of Mixtures; (1)Methanol, (2) Ethylene Glycol, (e) Propylene Glycol.

Table II. Comparison of Analyses of Various Samples of PET/PT's by Gas Chromatography and NMR.

Copolyester Sample	Observed area of PG's in gas chromatogram, %.	Mole % of PT units by GC	Mole % of PT units by NMR
EP-2	15.8	13.8	14.2
EP-3	18.2	15.9	17.6
EP-4	24.1	20.1	20.8

PG;propylene glycol
PT unit; propylene terephthalate unit
GC;gas chromatography

In the procedure of the gas chromatographic analysis of the PET/PT, as similar as in the determination of diethylene glycol units in PET,¹³ the copolyester was saponificated and filtered. The mixture of the liberated glycols was injected into the gas chromatography under the described conditions.

The typical chromatogram of the mixture of EG and PG is shown in Fig. 3., which indicates the complete separation of EG from PG under the operating conditions.

The assignments of the peaks in the chromatogram were made comparing with the retention times of the known compounds. Peaks 1, 2 and 3 are readily assigned to be methanol, EG, and PG, respectively.

Calibration curve was established by preparing a series of mixtures of EG and PG, diluting these mixtures approximately thirty-fold with methanol, and injecting 1 μ l of each standard into the gas chromatography.

The composition of the copolyester was determined by the calibration curve. The results of these analyses are shown in Table II.

Table II lists the mole per cent of PT units determined by gas chromatographic analysis compared with those by NMR analysis. The

data show all the values are in close agreement, though the values determined by gas chromatography are lower than those by NMR. This difference may be due to the loss of glycols during the pre-treatments, i.e., saponification and purification before injecting the filtrate into the gas chromatography.

2. Copolyesters of dimethyl terephthalate with ethylene glycol and polyethylene glycol-400.

The chemical structure of the PET/(PEG-400)T is shown in Fig. 4., where x and y are the mole fractions of the ET units and polyethylene glycol-400 terephthalate (PEGT) units in the copolyester, respectively. P is the average number of ethylene oxide units in PEG-400.

In case of PET/(PEG-400)T, there are three kinds of protons; (a) phenylene protons, (b) protons of methylene group-COO-CH₂-C-, mainly due to ethylene glycol, and (c) protons of methylene group -C-CH₂-O-C-, mainly due to polyethylene glycol. Thus, three kinds of peaks are expected to be appeared in the spectrum of PET/(PEG-400)T.

Since the polymer has a high enough molecular weight, the effects of end groups can be

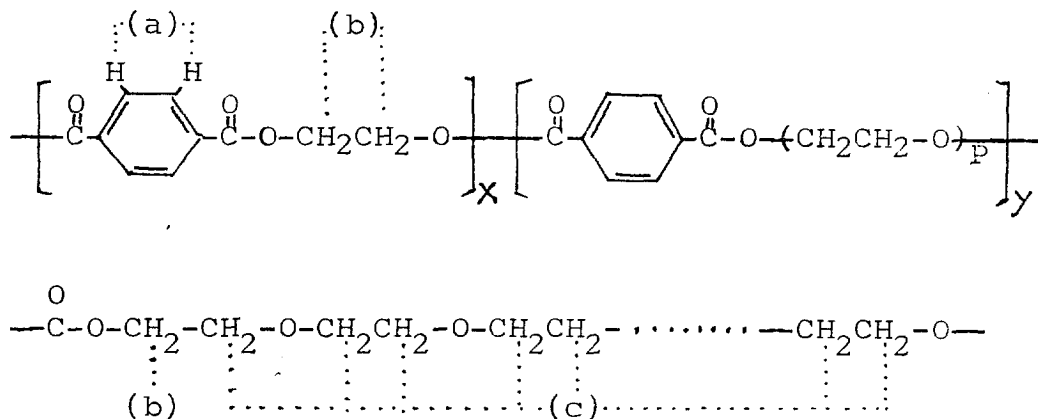


Figure 4. Structure of Copolyester of Dimethyl Terephthalate with Ethylene Glycol and Polyethylene Glycol-400.

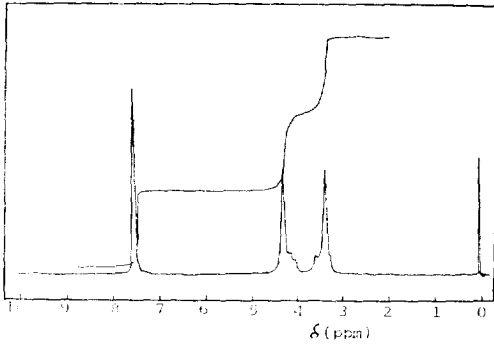


Figure 5. NMR Spectrum of PET/(PEG-400)T; 84/16, Molar Ratio of Feed Monomer, in Trifluoroacetic acid (0.1 g/ml) at Room Temperature.

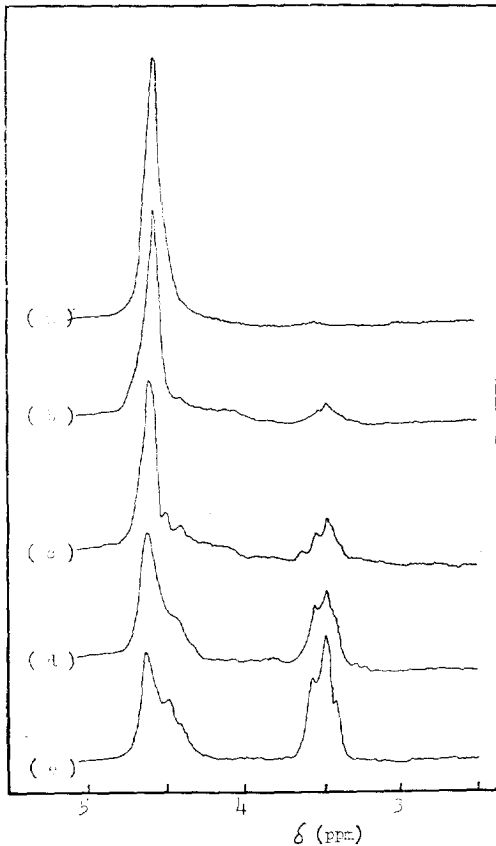


Figure 6. Methylene Peaks in NMR Spectra of PET/(PEG 400)T: (a) PET, (b) PET/(PEG-400)T (95/5, Molar Ratio of Feed Monomer), (c) 92/8, (d) 88/12, (e) 80/20.

neglected.

The characteristic spectrum of PET/(PEG-400)T is shown in Fig. 5. In Fig. 5., as expected above, three resonance peaks are appeared. The peak at 7.6 ppm is due to the protons of phenylene group (a), and the peak at 4.5 ppm is due to the two equivalent protons of $-\text{COO}-\text{CH}_2-\text{C}-$ (b), while the peak at 3.4 ppm is due to the protons of $-\text{C}-\text{CH}_2-\text{O}-\text{C}-$ (c). The very similar chemical shifts were also observed in the previous work on copolyesters made from DMT with EG and diethylene glycol by Harada and Ueda¹⁴.

Fig. 6. shows the spectra of several PET/(PEG-400)T's with different PEGT unit contents. The intensities of the peaks in the region of 3.3~3.5ppm increase and those in the region 4.3~4.5ppm decrease with increasing amount of PEGT units in the copolyester.

The peaks in the region of 4.3~4.5ppm and 3.3~3.5ppm are mainly due to the protons of ET units and PEGT units, respectively, in the copolymer chain. Therefore, the relative intensities of these resonance peaks can be used to determine the composition of the copolyester.

Taking into account the number of protons in the ET and PEGT units, the integrated intensities of those resonance peaks follow the equation;

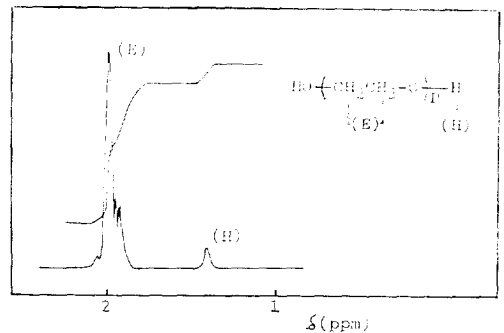


Figure 7. NMR Spectrum of PEG-400 in Benzene by 5% Solution. Cyclohexane (2%) was Used as an Internal Standard.

$$\frac{A_b}{A_c} = \frac{4x+2y}{y(4P-2)} = \frac{4-2y}{y(4P-2)} \dots (2)$$

where, A_b and A_c are the resonance peak areas of the methylene proton (b) and methylene proton(c), respectively.

In order to determine the composition of the copolyester by equation(2), it is necessary to determine the average number, P, of ethylene oxide units in PEG-400. P can be also determined by NMR spectroscopic method previously described.

The structure of PEG-400 is $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_p\text{-H}$, and there are two kinds of protons in the molecule, i.e., hydroxy and methylene protons. In case of PEG-400, the resolution of the end group from the polymer chain is difficult, while Liu¹⁵ employing benzene as a solvent, was able to resolve the end group of the polymer chain. The NMR spectrum of PEG-400, in benzene is shown in Fig. 7.

The ratio of the integration of $-\text{OH}$ proton resonance peak (1.4 ppm) to that of $-\text{O}-\text{CH}_2\text{C}-\text{H}_2\text{O}-$ proton resonance peak (2.0ppm) follows the equation;

$$\frac{A_H}{A_E} = \frac{2}{4P} \dots \dots \dots (3)$$

where A_H and A_E are the resonance peak areas of hydroxy and methylene protons, respectively.

The P of PEG-400 is calculated to be 8.5, and the number average molecular weight is to be 392. This shows a good agreement with the molecular weight which is claimed to be 400 by the maker.

On substituting the value P into equation (2), we obtain the following equation;

$$\frac{A_b}{A_c} = \frac{4-2y}{y(4 \times 8.5-2)} \dots \dots \dots (4)$$

Hence, the mole fraction of the PEGT units in the copolyester can be calculated from the equation (4) with the NMR peak integrations.

The contents of PEGT units obtained from NMR spectra and the feed compositions of the copolyester samples are given in Table III.

In Table III, there is slight difference between the composition of the feed and that from NMR spectra. And this difference is increased with increasing content of PEGT units.

Since the side reaction product, e.g., diethylene glycol units, formed during the polycondensation is negligible, the difference may be due to the following reasons. As the reactivity of PEG-400 with DMT is less than that of EG, PEG-400 in the feed might not be reacted completely with DMT. And, though PEG-400 in the feed reacted with DMT completely, a portion of terminal PEGT units of the oligomer,

Table III. Composition of PET/(PEG-400)T by NMR Analysis

Copolyester Sample	A_b (arb. unit)	A_c (arb. unit)	PEG-400 Content		(2)-(1)
			(1); in Copolyester by NMR	(2); in Mono-mer Feed	
EPO-1	352.0	45.4	1.6	2.0	0.4
EPO-2	312.4	96.8	3.8	5.0	1.2
EPO-3	289.2	160.4	6.7	8.0	1.3
EPO-4	220.2	189.3	10.2	12.0	1.3
EPO-5	203.9	241.9	13.8	16.0	2.2
EPO-6	153.2	223.3	16.7	20.0	3.7
EPO-7	148.6	290.8	21.8	26.0	4.2

PEG-400; polyethylene glycol-400

A_b ; Area of the methylene proton peak (b) at 4.3 ppm.

A_c ; Area of the methylene proton peak (c) at 3.4 ppm.

prepared to proceed polycondensation, might diffuse out of the reaction vessel as a condensate during the polycondensation step under extremely reduced pressure.

CONCLUSION

The composition of ethylene glycol-propylene glycol-terephthalate copolyester, PET/PT, containing whole range of propylene terephthalate unit contents, and the composition of ethylene glycol-polyethylene glycol-400-terephthalate copolyester, PET/(PEG-400)T, containing less than 30 mole% of polyethylene glycol-400 terephthalate unit contents were determined by high resolution NMR spectroscopic method in trifluoroacetic acid solution.

The composition of PET/PT can be determined from the ratio of the area of the resonance peak at 7.6 ppm to that at 1.0~1.2 ppm, i.e., the ratio of phenylene protons to methylenes.

The composition of PET/(PEG-400)T can be determined from the ratio of the area of the resonance peak at 3.3~3.5 ppm to that at 4.3~4.5 ppm, assigned to be ether- and ester-linked methylene protons, respectively.

The results were confirmed by gas chromatographic method.

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