

Copolyesters. I. Sequence Distribution of Poly(butylene Terephthalate-co-Adipate) Copolyesters Determined by 400 MHz NMR

INTRODUCTION

The chemical structure (random, alternative, or block) of copolymers is an important factor in determining their final properties. For copolyesters, nuclear magnetic resonance spectroscopy (NMR) is a powerful technique for qualitative and quantitative analysis of their chemical structure.¹⁻¹¹ Yamadera and Murano showed that the degree of randomness of some copolyesters could be determined by NMR.¹ These analyses can be done only if the resonance signals of given proton(s) or carbon(s) with different sequences have different chemical shifts. It has been shown that the aromatic protons of the terephthalate unit of copolyesters with different aromatic and aliphatic diol sequences have different resonance signals.²⁻⁴ The resonance signal of aromatic carbons of copolyesters of terephthalic acid, ethylene glycol, and 1,4-butanediol was found to give a quartet.⁵ Also, the resonance signal of proton(s) or carbon(s) of the glycol unit of copolyesters with different diacid sequences was observed to give different chemical shifts^{1,6-11} and thus the sequence distributions could be determined.

The chemical shifts of α -methylene protons of the butylene unit of poly(butylene terephthalate) and poly(butylene adipate) were found to be different. It is possible to differentiate the different sequences of copolyesters of poly(butylene terephthalate) and poly(butylene adipate) by proton NMR. In this paper, we present the analysis of sequence distributions of these copolyesters.

EXPERIMENTAL

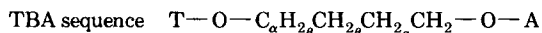
Terephthalic acid was obtained from Far Eastern Textile Ltd., Taiwan and adipic acid was supplied by ICI. 1,4-Butanediol and tetrabutyl orthotitanate were Merck reagent grade. The copolyesters of terephthalic acid, adipic acid, and 1,4-butanediol were prepared by a method similar to the procedure of Droke and co-workers¹² with tetrabutyl orthotitanate as the catalyst. The intrinsic viscosity at 30°C in phenol/tetrachloroethane (60/40 wt/wt) of each copolyester was slightly greater than 0.6 dL/g. The composition of the copolyesters is characterized by the molar ratio of adipic acid to terephthalic acid, e.g., the copolyester with molar ratio of adipic acid to terephthalic acid equal to 45:55 is denoted as A45.

The proton NMR spectra of the copolyesters in CF_3COOD were determined by Bruker AM 400 NMR by using tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

The proton NMR spectra of poly(butylene terephthalate) (PBT), poly(butylene adipate) (PBA), and copolyester A45 are shown in Figure 1. The resonance peaks are assigned for each polyester as shown in Table I. The resonance peaks of butylene protons of A45 are interesting: quartet was found for α -methylene protons and triplet for β -methylene protons.

By comparing with the resonance peaks of PBT and PBA, the resonance signals of α -methylene protons of A45 with four possible sequences can be assigned. The α -methylene protons with TBT, TBA, ABT, and ABA sequences resonated at 5.09, 5.02, 4.82 and 4.77 ppm, respectively, where T is the terephthalate unit, B is the butylene unit, and A is the adipate unit.



The resonance peaks of β -methylene protons of A45 exhibited triplet. The chemical environments of β -methylene protons with TBA and ABT sequences are not identical, but the difference is insignificant, so that a single peak was found for these two heterolinkages due to the overlap of resonance peak. The chemical shifts of β -methylene protons of TBT, ABA, and TBA(ABT) sequences are located at 2.59, 2.32, and 2.45 ppm, respectively.

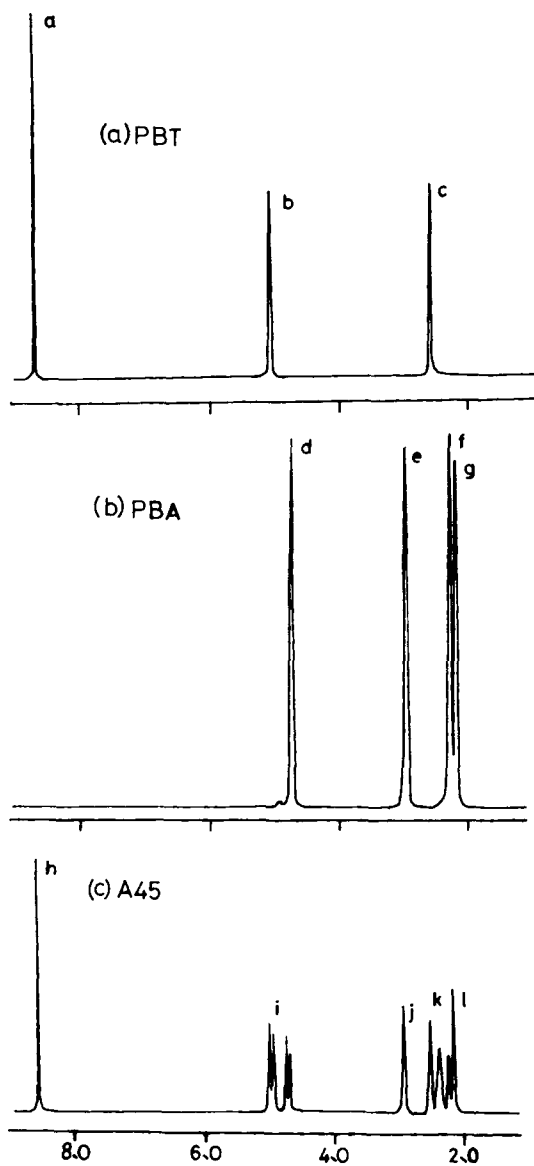


Fig. 1. NMR spectra of PBT, PBA, and A45.

The quartet data are used here to determine the sequence distributions and degree of randomness of the copolyesters. The expanded NMR spectra from 4.6 to 5.3 ppm for the copolyesters are shown in Figure 2.

The molar fractions of terephthalate (X_T) and adipate (X_A) can be obtained from the intensities of the quartet, that is,

$$X_T = (I_{TBT} + I_{TBA})/S \quad (1)$$

$$X_A = (I_{ABT} + I_{ABA})/S \quad (2)$$

where I_{TBT} , I_{TBA} , I_{ABT} (where $I_{TBA} = I_{ABT}$), and I_{ABA} represent the integrated intensities of

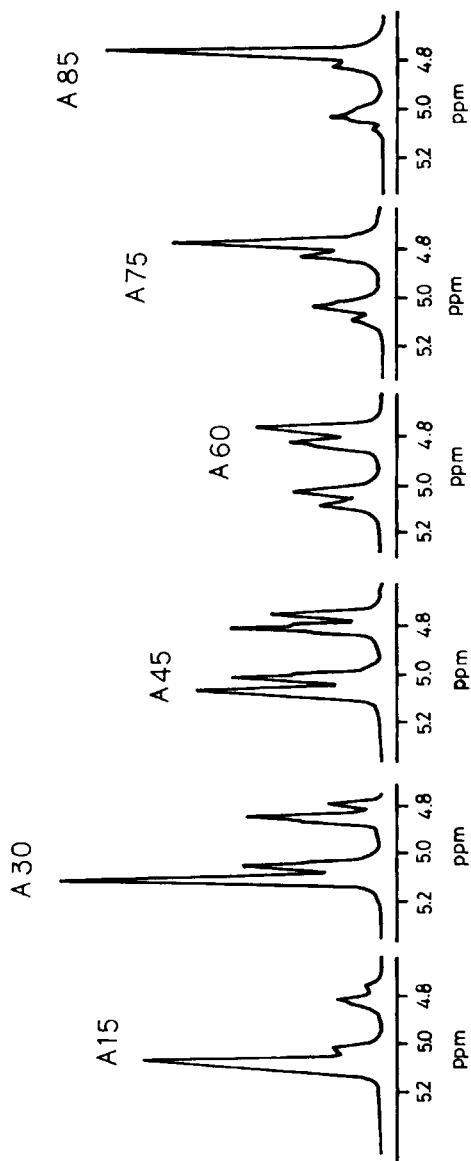


Fig. 2. Expanded NMR spectra of copolyesters.

TABLE II
Molar Fraction of Adipate, Number Average Sequence Length, and Degree of Randomness
Determined by NMR Analysis

	X_A	\bar{L}_{nT}	\bar{L}_{nA}	B
A15	0.17	6.25	1.25	0.96
A30	0.29	3.03	1.41	1.04
A45	0.44	2.08	1.82	1.03
A60	0.59	1.59	2.44	1.04
A75	0.76	1.33	3.57	1.03
A85	0.83	1.11	6.25	1.06

CONCLUSION

The proton NMR spectra of copolyesters of poly(butylene terephthalate) and poly(butylene adipate) were determined by 400 MHz NMR. The chemical shifts of α -methylene protons and β -methylene protons in the butylene unit with different sequences were found to be different. The sequence distributions and degree of randomness were determined through analysis of quartet of α -methylene protons. It was found that the copolyesters were random copolymers with degree of randomness equal to about 1.

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