Sequences of Copolyesters by ^{1}H NMR and ^{31}P NMR Spectroscopy

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ABSTRACT: ^{31}P NMR and ^{1}H NMR spectra of copolyesters containing phosphorus compounds, obtained by ester-exchange reaction, were studied. Poly(ethylene terephthalate) was used as the main component and poly(hydroquinone phenylphosphate), poly[bis(4-hydroxyphenyl)sulfonephenylphosphate], and poly[bis(4-hydroxyphenyl)sulfonemethylphosphate], as phosphorus compounds. The sequence distribution can be elucidated by ^{31}P NMR as well as ^{1}H NMR, and two polyesters become to random distribution by ester-exchange reaction between two polyesters.
KEY WORDS ^{1}H Nuclear Magnetic Resonance / ^{31}P Nuclear Magnetic Resonance / Copolyesters / Randomcopolymer / Phosphorus Compounds / Ester-Exchange Reaction /

Recently, flame-retardant polymers have been studied for safety, and as phosphorus-containing flame retardants for use in place of those containing halogen to ensure their environment protection and public security.

To ensure its flame-retardancy, it is better to be chemically bonded to the polymer main chains.

As for the ester-exchange, Kresse explain in detail.[1]

The sequences of various copolyesters have been elucidated by the present authors[2-4] and others[5,6] using ^{1}H NMR spectroscopy. Ester-exchange reactions between two polyesters has also been studied[4] and random copolyesters were obtained by ester-exchange reaction under melting. In ^{1}H NMR spectrum, differences in chemical shifts between these sequences are generally very small and it is quite difficult to make clear the sequence distributions of these copolymers. But in some cases, differences in chemical shifts between these sequences are fairly large. For instance, in the polyethyleneterephthalate–sebacate copolymer, ethylene glycol protons show three peaks, corresponding to terephthalate–ethylene glycol–terephthalate, terephthalate–ethylene glycol–sebacate, and sebacate–ethylene glycol–sebacate sequences from the lower magnetic field. They have fairly large chemical shift difference and their sequence distributions have been studied in detail.

Furthermore, Chûjô et al.[8] succeeded to expand the small chemical shifts using some NMR shift reagents.

^{31}P NMR spectroscopy is more useful for studying phosphorus compounds, because of the large chemical shifts and 100% natural abundance of ^{31}P, but very few studies of ^{31}P NMR have been done on synthetic polymers in spite of their industrial importance.

In the present paper, the chemical structure of the copolymers from phosphonic acid is elucidated by ^{31}P NMR. Poly(ethylene terephthalate) (PET) is blended with other polyesters having the phosphonic acid unit, such as poly(hydroquinonephenylphosphate) (PQPP), poly[bis-(4-hydroxyphenyl)sulfonephenylphosphate] (PSPP), and poly[bis(4-hydroxyphenyl)sulfonemethylphosphate] (PSMP), under melting condition. These two polyesters undergo the ester-exchange reaction, and produce the copolyester. These ester-exchange reactions are followed by ^{31}P NMR spectroscopy, which is more advantageous than ^{1}H NMR due to large chemical shifts.

EXPERIMENTAL

The polyesters used in the experiment were as follows:
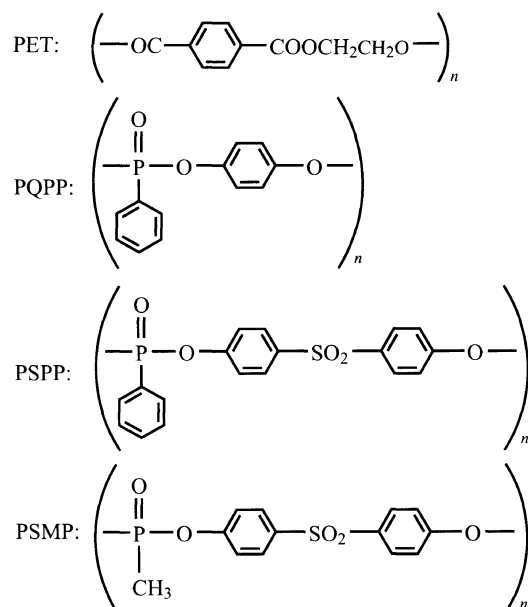
PQPP, PSPP, and PSMP were blended with PET at 275°C under nitrogen for certain times in a reaction tube.

^{31}P NMR spectra were measured in a p-chlorophenol/tetrachloroethane (2:3) mixed solvent at 70°C with a JEOL JNM-PET-100 (Fourier Transformed NMR) at 40.481 MHz. H_3PO_4 was used as the internal standard and D_3PO_4 as the rock-signal.

^{1}H NMR spectra of these copolymers were measured in trifluoroacetic acid solution at 70°C with a Varian HA-100 Spectrometer, for assigning what in the ^{31}P NMR spectra.

Melting points were measured with a Perkin-Elmer DSC.

Intrinsic viscosity of some copolymers was measured by the ordinary method using phenol/1,1,2,2-tetrachloroethane (60:40 by weight) as the solvent at 25°C.

RESULTS AND DISCUSSION

Copolyester from PET and PQPP

^{1}H NMR spectra of this copolyester are shown in Figure 1. Phenyl protons of the terephthalate unit show three peaks, for E-T-E , E-T-Q , and Q-T-Q sequences from the higher magnetic field, at about 2 ppm (τ-value), and ethylene protons of glycol units show also three peaks, for P-E-P, P-E-T, and T-E-T sequences from the higher magnetic field at about 5.5 ppm. Differences in chemical shifts among these two peaks are quite small, about 0.1 ppm.

The ^{31}P NMR spectrum is shown in Figure 2. Three peaks are observed at 12.765, 16.761, and 20.581 ppm from H_3PO_4. PQPP has single peak at 12.765 ppm and poly(ethylenephenyl phosphate) has a single peaks at 20.581 ppm. Therefore these three peaks are assigned to Q-P-Q, Q-P-E, and E-P-E sequences. They have fairly large chemical shifts' differences.

From these spectra, the degree of randomness is obtained as,

$$D = \frac{4 f_{Q\text{-}P\text{-}Q} f_{E\text{-}P\text{-}E}}{(f_{Q\text{-}P\text{-}E})^2}$$

where $f_{Q\text{-}P\text{-}Q}$, $f_{Q\text{-}P\text{-}E}$, and $f_{E\text{-}P\text{-}E}$ are the fractions of Q-P-Q, Q-P-E, and E-P-E peaks in the area of the three peaks in ^{31}P NMR spectrum, respectively.

At $D = 1$, P is distributed randomly in PET chain.

The change of D value with reaction condition was studied. 95.7% PET and 4.3% PQPP are blended at 275°C and D values are obtained from ^{31}P NMR spectra. E-P-E peak increased and Q-P-Q decreased with reaction time. As shown in Figure 3, D value decreased with reaction time, and P unit look on nearly random distribution by blending.

We measured melting point of the blended copolymers by DSC. In Figure 4, the relationship between D value and melting points of these copolymers is shown. They are in fairly good correlation.

The acid value of PET, catalyst, and contents of phosphour affect the ester-exchange reaction rate.[9]

During the studies on these blended copolymers, it is found that intrinsic viscosity of copolymer increases at the initial stage of the reaction and then decreases with reaction time, which is derived from degradation by heating.

As shown in Figure 5, in 5 min blended copolymer, Q-P-E peak is larger than E-P-E peak, on the other hand, in 20 s blended copolymer, the E-P-E peak was larger than Q-P-E peak.

At the initial stage of reaction, E-P-E peak should be smaller than Q-P-E, if the E-P-E sequence is formed by way of Q-P-E sequence.

Intrinsic viscosity of the starting PET is 0.60, that of the copolymer at the initial stage (20 s) increases to 0.69, and then decreases to 0.62 by 5 min blending. This indicates that phosphorus is attacked by the –OH group of ethylene glycol unit in PET chain end from both side, simultaneously, and forms a higher molecular weight copolymer. After that reaction, ester-exchange reaction takes place and PET and PQPP becomes random copolymer.
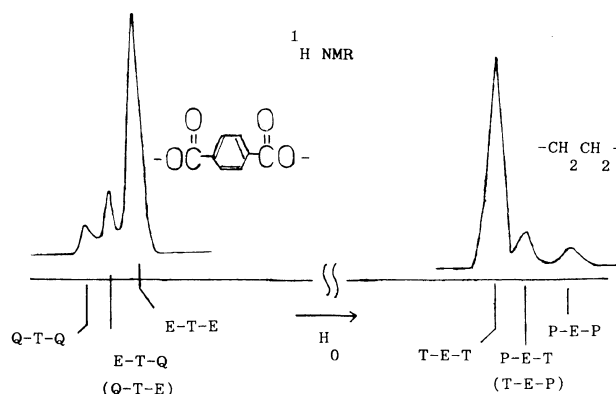
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Figure 1. ^{1}H NMR spectrum (100 MHz) of the blended copolymer of PET and PQPP.
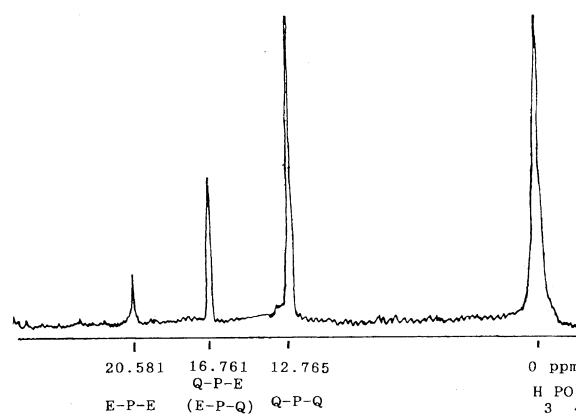

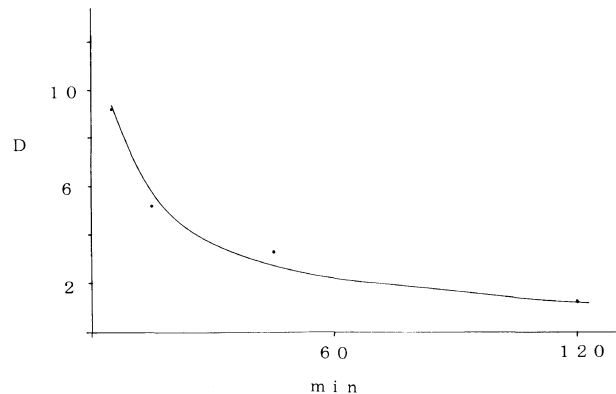Figure 2. ^{31}P NMR spectrum of the blended copolymer of PET and PQPP.

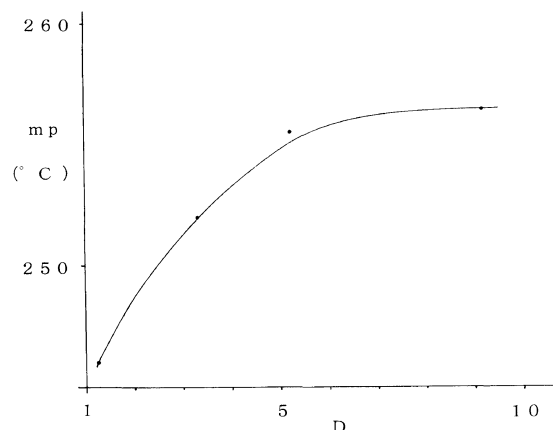Figure 3. Change in D value with the reaction time at 275°C (95.7 mol% PET and 4.3 mol% PQPP).

Figure 4. Relationship between D value and melting point (95.7 mol% PET and 4.3 mol% PQPP).
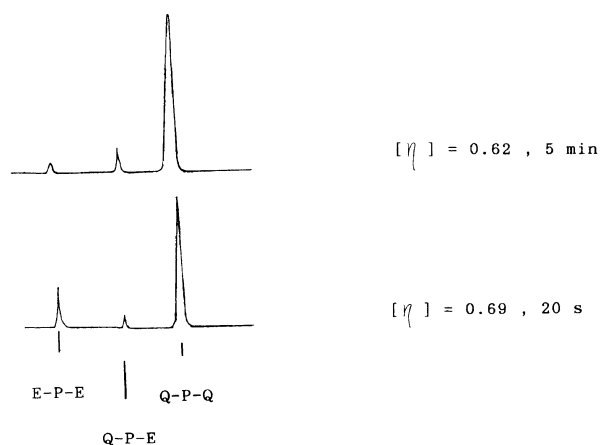
$[\eta] = 0.62$, 5 min

$[\eta] = 0.69$, 20 s

E-P-E

Q-P-Q

Q-P-E

Figure 5. ^{31}P NMR spectra of the blended copolymers of PET and PQPP at the start of the reaction.

Copolyester from PET and PSPP

Ester-exchanged copolyester from PET and PSPP was also studied by ^{1}H NMR and ^{31}P NMR.

In ^{1}H NMR, phenyl and ethylene glycol protons show three peaks, respectively, assigned to E-T-E, E-T-P, and P-T-P sequences from the higher magnetic field, and T-E-T, T-E-P, and P-E-P sequences from the lower magnetic field. The differences in chemical shifts of these three peaks are very small.

In ^{31}P NMR, three peaks are found at 12.797, 16.898, and 20.819 ppm from phosphoric acid and assigned to S-P-S, S-P-E, and E-P-E linkages. From these peaks, randomness of the copolymers is obtained in the same way as in previous section.

Copolyester from PET and PSMP

Ester-exchanged copolymers from PET and PSMP is also studied by ^{1}H NMR and ^{31}P NMR spectroscopy.

And almost same results are obtained as in previous sections.

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