Preparation of an Acrylics-Grafted Polyester and Its Aqueous Dispersion—Structural Study of Acrylics-Grafted Polyesters

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ABSTRACT: Structural study of two grafted polyesters, which were different in mechanical properties, was investigated by DMA, TEM, and high-resolution solid-state ^{13}C-NMR. Using DMA and TEM, a separated phase larger than 100 nm was not found in the grafted polyesters. The main chain and the side chain seemed miscible. Analysis of $T_{1\rho H}$s and their distributions made the difference of microstructure in the grafted polyesters clear. P(EA-AA)-grafted polyester, which was very brittle, had a separated phase in the grafted polyester. The separated phase was estimated to be at a size of about 3 nm. On the other hand, P(St-DEF-MAnh)-grafted polyester, which was very ductile, had a homogeneous microstructure. The difference in the microstructures of the grafted polyesters seemed to effect the mechanical properties of the grafted polyesters. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 392–402, 2000

Key words: grafted polyester; NMR; relaxation time; phase separation; mechanical property

INTRODUCTION

The reduction of volatile organic compounds and CO_2 has been receiving intensive attention, and the reduction of the solvent emission from organic coatings such as paints and adhesives has been considered for about 20 years.[1] High-solids coatings, powder coatings, and water-borne coatings have been developed to replace conventional solvent-borne coatings; however, these coatings involved several problems,[2] for example, high-solids coatings still contain some solvents, powder coating systems need a breakthrough in the control of the film thickness, and even water-borne coating systems have some problems. Among these coatings, water-borne coatings are most preferable because of the compatibility of conventional coating systems.

As conventional water-borne coatings, acrylic emulsions, produced by emulsion polymerization, are widely used. For high demands, high-performance water-borne coatings like epoxy emulsions,[3,4] polyester dispersions,[5,6] and polyurethane dispersions[7] are extensively used.

The methods to disperse these resins in aqueous media are: (1) mechanical emulsification, and (2) self-emulsifying by introduction of hydrophilic groups into the molecules of resins. In the former method, the water resistance and adhesion of the coatings obtained from the dispersion are reduced because emulsifiers migrate to the surfaces and interfaces. To avoid the use of emulsifiers, polyesters are copolymerized with hydrophilic monomers. In the case of linear high molecular-weight

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Table I   Comparison of Mechanical Properties of the Grafted Polyesters

	Tensile Strength (kgf/cm^2)	Tensile Elongation at Break (%)	Compatibility Rating between the Main Chain and the Side Chain[a]
Raw polyester	500	3.0	—
Polyester-g-P(EA-AA)[b]	130	1.0	1
Polyester-g-P(St-DEF-MAnh)[c]	550	3.0	5

[a] Compatibility rating: good = 5, medium = 3, bad = 1.
[b] The mass ratio of polyester/ethyl acrylate (EA)/acrylic acid (AA) is 75/10/15.
[c] The mass ratio of polyester/styrene (St)/diethyl fumarate (DEF)/maleic anhydride (MAnh) is 75/10/10/5.

polyesters, sodium 5-sulfoisophthalic acid[8] or polyethylene glycol[9] or hydrophilic monomers are often copolymerized. However, the copolymerization increases the melt viscosity, and decreases water resistance and adhesion.

We have developed a new class of water-borne polyesters that are dispersible without using additional emulsifiers. These water-borne polyesters are of the acrylics-grafted type, and form stable aqueous dispersions. They consist of "core-shell" particles with a core of high molecular-weight polyester. In previous articles, we discussed the preparation and the characterization of an acrylics-grafted polyester and its dispersion, i.e., the effect of the grafting conditions, reactivities of the grafting monomers, the grafting solvents,[10] the grafting methods[11] on the molecular structures of the grafted polyesters, the particle structures,[13] the particle diameters of their dispersions,[10] and the dispersion viscosity and the dispersion rheology.[12] We discussed the mechanical properties of the acrylics-grafted polyesters to make the factor effecting the mechanical properties clear in our previous article.[14] The mechanical property of the acrylics-grafted polyesters was effected by the composition of the grafted side chain (the acrylic segments), not the molecular weights of the grafted side chain or the content of the grafted side chains in grafted polyesters. Results are shown in Table I.

Nuclear magnetic resonance (NMR) is one of the most suitable methods to study molecular motions of polymer chains. There have been a lot of studies on the compatibilities of polymer blends by relaxation behavior of pulse NMR. High-resolution NMR shows molecular mobilities in terms of line shape and relaxation time. Recently, there have been many studies on molecular motions of polymer chains in the solid state in relation to relaxation time of solid-state high-resolution NMR. Relaxation time and spin-diffusion have been applied to studies on morphology of inhomogeneous polymer systems, such as the crystalline/amorphous behavior of polymer blends. Spin-lattice relaxation time of ^{1}H and spin diffusion have especially been applied to many studies on polymer blends. In this article, we report the difference of the structures of films obtained from two grafted polyesters that were different in mechanical properties. A structural study of the grafted polyesters was investigated by high-resolution solid-state ^{13}C-NMR.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), ethylene glycol (EG), and neopentyl glycol (NPG) were of commercial grade. Other reagents were of reagent grade, and all reagents were used without further purification.

Preparation of Polyester

DMT (466.0 g), DMI (466.0 g), EG (443.0 g), NPG (401.0 g) and t-n-butyl titanate (0.52 g) were charged in a stainless steel autoclave equipped with a stirrer, a thermometer, and a refluxing condenser. Transesterification was carried out between 160 and 220°C for 4 h. After the reaction mixture was cooled to 200°C, fumaric acid (FA, 23.0 g) was added to the reaction mixture. Temperature was elevated from 200 to 220°C over 1 h for esterification. Finally, the temperature was raised to 255°C, and the pressure was gradually released over 1.5 h to 0.2 mmHg. The polyester obtained was pale yellow and transparent. It was used without further purification. The composi-

tion of the polyester was determined by ^{1}H-NMR as follows: terephthalic acid (TPA); 47 mol %: isophthalic acid (IPA); 48 mol %: FA; 5 mol %: EG; 50 mol %: NPG; 50 mol %.

Preparation of P(EA-AA)-Grafted Polyester

A polyester (60.0 g), methyl ethyl ketone (MEK, 72.0 g), and isopropyl alcohol (IPA, 18.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. The mixture was stirred under reflux (at 75°C) to dissolve the polyester. After complete dissolution of the polyester, a mixture of acrylic acid (AA, 12.0 g), ethyl acrylate (EA, 8.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (24.0 g), and IPA (6.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the grafted reaction product. To the solution of the grafted reaction product, triethylamine (20.2 g) was added to neutralize to it. Deionized water (160.0 g) was added to the neutralized mixture and stirred for 30 min. The remaining solvents and the excess of triethylamine were removed by distillation to obtain an aqueous dispersion. Ungrafted P(EA-AA) was removed by centrifugation (see below).

Preparation of P(St-DEF-MAnh)-Grafted Polyester

A polyester (60.0 g), methyl ethyl ketone (MEK, 72.0 g), isopropyl alcohol (IPA, 18.0 g), diethyl fumarate (DEF, 8.0 g), and maleic anhydride (MAnh, 4.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. The mixture was stirred under reflux (at 75°C) to dissolve the polyester. After complete dissolution of the polyester, a mixture of styrene (St, 8.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (24.0 g) and IPA (6.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the grafted reaction product. To the solution of the grafted reaction product, deionized water (10.0 g) was added to react with MAnh in the grafted side chain for 0.5 h under reflux, and cooled to room temperature. Triethylamine (TEA, 9.1 g) was then added to neutralize it. Deionized water (160.0 g) was added to the neutralized mixture and stirred for 30 min. The remaining solvents and the excess of triethylamine were removed by distillation to obtain an aqueous dispersion. Ungrafted P(St-DEF-

MAnh) was removed by centrifugation (see below).

Preparation of P(EA-AA)

Methyl ethyl ketone (MEK, 45.0 g) and isopropyl alcohol (IPA, 15.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. A mixture of acrylic acid (AA, 12.0 g), ethyl acrylate (EA, 8.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (15.0 g) and IPA (5.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the grafted reaction product. After the polymerization, the polymer was obtained by drying.

Preparation of P(St-DEF-MAnh)

Methyl ethyl ketone (MEK, 45.0 g) isopropyl alcohol (IPA, 15.0 g), maleic anhydride (MAnh, 4.0 g), and diethyl fumarate (DEF, 8.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. A mixture of styrene (St, 8.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (15.0 g) and IPA (5.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the grafted reaction product. To the solution of the grafted reaction product, deionized water (10.0 g) was added to react with MAnh in the grafted side chains for 0.5 h under reflux. After polymerization, the polymer was obtained by drying.

Molecular Weight

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of polymers were determined by GPC apparatus (Shimadzu Seisakusho. Inc., 6A series) using a column (Showa Denko Inc., KF80M 8 mm i.d. $\times$ 30 cm $\times$ 1, KF801 8 mm i.d. $\times$ 30 cm $\times$ 1, KF802 8 mm i.d. $\times$ 30 cm $\times$ 1). Measurements were carried out using a refractive index detector and tetrahydrofuran as a solvent. The column was calibrated using polystyrene standard samples of defined molecular weights. The results are shown in Table II.

Removal of Ungrafted Polymers

The solid concentration of the dispersion was adjusted to 10.0% using a mixed solution of a deion-

Table II Comparison of Physical Properties of the Grafted Polyesters

	M_w of Grafted Side Chain[a]	Water-Soluble Component[b] (%)	Polyester Content in Grafted Polyester[c] (%)	Grafted Polymer Content[d] (%)
Grafted polyester-1[e]	9000	20	94	27.5
Grafted polyester-2[f]	10,000	10	83	75

M_w of raw Polyester is 37,500 by GPC.
[a] Separation of the grafted side chains was carried out by hydrolysis of the grafting products.[13]
[b] Water-soluble components were obtained by ultracentrifugation.[13]
[c] Polyester contents were calculated, assuming that the water-soluble components consisted of ungrafted acrylics.
[d] Grafted polyester contents were calculated, assuming that one grafted polyester molecule consist of one polyester segment and one acrylics segment.
[e] The mass ratio of polyester/ethyl acrylate (EA)/acrylic acid (AA) is 75/10/15.
[f] The mass ratio of polyester/styrene (St)/diethyl fumarate (DEF)/maleic anhydride (MAnh) is 75/10/10/5.

ized water and isopropyl alcohol (50/50). The dispersion was centrifuged by an ultracentrifuge (Hitachi Koki Inc., automatic preparative ultracentrifuge model 55P-72) with a rotor (Hitachi Koki Inc., RP50T-2). Centrifugation was carried out under an average centrifugation at $82,000 \times g$ for 2 h. After centrifugation, the supernatant fraction was dried at 120°C for 2 h. The solid concentration of the supernatant fraction was calculated gravimetrically. The amount of the water-soluble components was calculated from the solid concentration of the supernatant fraction. The grafting product after removal of water-soluble components was diluted until the solid concentration of the grafting product was ca. 30%. By leaving the grafted polymer under stirring for 24 h, the grafted polymer was dispersed in water. Mass ratios of the main chain to the side chain were calculated from the amount of water-soluble components. Results are shown in Table II.

Mechanical Property

The mechanical property was measured using a tensile tester (Orientec Corporation, RTM-100). The condition was as follows: sample, $10.0 \times 40.0 \times 0.05$ mm; crosshead speed, 100 mm/min.

Dynamic Mechanical Analysis (DMA)

DMA was carried out using a DMA tester (Rheology Co., Ltd., DVE-V4). The condition was as follows: sample, $4.0 \times 15.0 \times 0.02$ mm; heating rate, 4°C/min; frequency, 110 Hz.

Compatibility

The polymers forming the main chain and the side chain in the grafting products were separately synthesized. Each polymer was dissolved in tetrahydrofuran to form transparent solutions having a solid concentration of 5%. The polymer solutions were mixed together at a mass ratio of 50/50. The mixture was applied to a glass plate and dried at 120°C for 10 min to obtain a coating film thickness of 0.1 mm. The transparency of the coating film was visually observed. When the coating film had high transparency, the compatibility rating was 5. When the coating film was turbid, the compatibility rating was 3. When the coating film was white, the compatibility rating was 1.

Nuclear Magnetic Resonance (NMR)

High-resolution solid-state ^{13}C-NMR measurements were made with a Varian XL-300 spectrometer at a resonance frequency of 75.5 MHz. It was performed by the crosspolarization (CP)/ magic angle-spinning (MAS) technique together with the high-power dipolar decoupling (DD) technique. Proton spin-lattice relaxation times in the laboratory and rotating frames, T_1 and T_{1r}, were measured through high-resolved ^{13}C resonances by the CP technique.

RESULTS AND DISCUSSION

We have previously discussed the molecular structure of the two grafted polyesters.[13] These polyesters formed transparent films. These results showed that there was no separated phase larger than 100 nm in the films. In this article, we used a method where phase separations smaller than 100 nm can be detected.
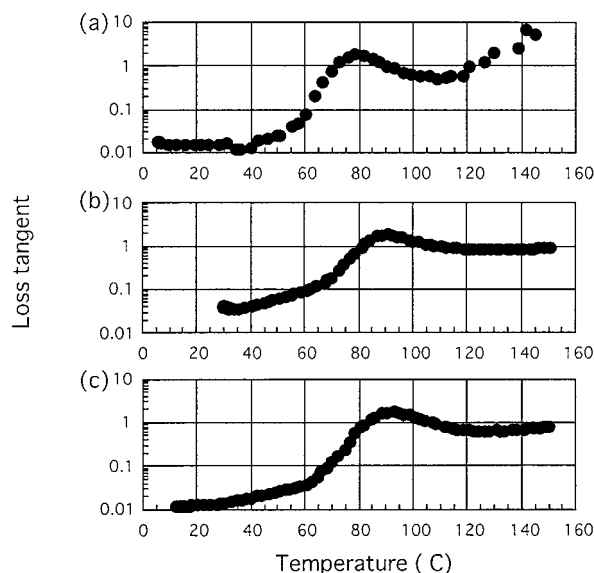
Figure 1 DMA results. (a) Raw polyester: (b) P(EA-AA)-grafted polyester: (c) P(St-DEF-MAnh)-grafted polyester.

DMA Study

Figure 1(a), (b), and (c) shows the DMA results of the raw polyester, P(EA-AA)-grafted polyester and P(St-DEF-MAnh). The analysis of P(EA-AA) or P(St-DEF-MAnh) homopolymer could not be made, because these polymers were very brittle. In each figure, the maximum of the loss tangent was 1. This means that no phase separation was observed in all the films. Compared with the raw polyester, the maximum of the loss tangent of each grafted polymer moved to a high temperature. This was due to the decrease in the mobility of the main chain caused by grafting of the side chain. From the above, no difference in the microstructure of the grafted polyesters could be observed. In addition, no difference between the films obtained from the P(EA-AA)-grafted polyester and that from the P(St-DEF-MAnh)-grafted polyester could be observed in transmission electron microscopy (TEM). This means that there was no separated phase larger than 100 nm in the films. The samples were prepared as follows: the dispersions were diluted with deionized water and dried at 120°C for 2 h. The samples were then stained with ruthenium tetraoxide (RuO₄) according to Trent's method.[15] It is well known that RuO_4 is a strong oxidizing agent, and is able to stain aromatic polyesters. Therefore, the TEM image shows the polyester with dark phases.

Proton T_1 (T_{1H})

Figure 2(a) and (b) shows the ^{13}C-NMR spectra of two grafted polyesters. The phenylene carbon in TPA or IPA and the ethyl carbon in EA or DEF were used for T_{1H} determinations of the grafted polyesters. Figure 3(a) and (b) shows the results of the proton inversion-recovery crosspolarization measurements of the main chain (polyester segments) and the side chain (acrylics segments) of the P(EA-AA)-grafted polyester, respectively.

They were plotted as ln $M_0 - M(t)$ vs. delay time in Figure 4(a). Here, M_0 and $M(t)$ were the initial intensity and the intensity at the decay time of t s. In the case of P(St-DEF-MAnh)-grafted polyester, the same procedure was carried out [Fig. 4(b)]. Table III shows the T_{1H} values for the main chain and the side chain in the grafted polyesters. From the results, the main chain and the side chain in each grafted polymer had almost the same T_{1H} values. If the heterogeneous structure is formed, the maximum diffusion path length (L) are determined from the spin diffusion constant (D) and the T_{1H} value (t) according the following equation:

$$\langle L^2 \rangle \sim 6Dt \qquad (1)$$

For the present system D is not known, but we may use the approximation $D \sim \langle L_0^2 \rangle / T_2$, where l_0 is the distance between protons, and T_2 is the proton spin-spin relaxation time.[16] From the value of t (~ 1.9), T_2 (~ 10 μs) and l_0 (~ 0.1 nm), eq. (1) gives a value for the root-mean-square pathlength of 33 nm. This means that there was no separated phase larger than 33 nm in the grafted polyesters.

Proton $T_{1\rho}$ ($T_{1\rho H}$)

To investigate phase separation smaller than 50 nm in size, $T_{1\rho H}$ was determined. In this study, the methyl carbon in NPG and the methylene and methine carbon in the side chain were used for $T_{1\rho H}$ determinations.

Figure 5 shows the change of the signal intensity during the crosspolarization contact time for the raw polyester. The values were approximated by the 11th-dimensional least-squares method, and the decay time distribution was obtained. Two peaks seemed to exist from the results of the approximation. A two-dimensional least-squares method was carried out. The results are shown in
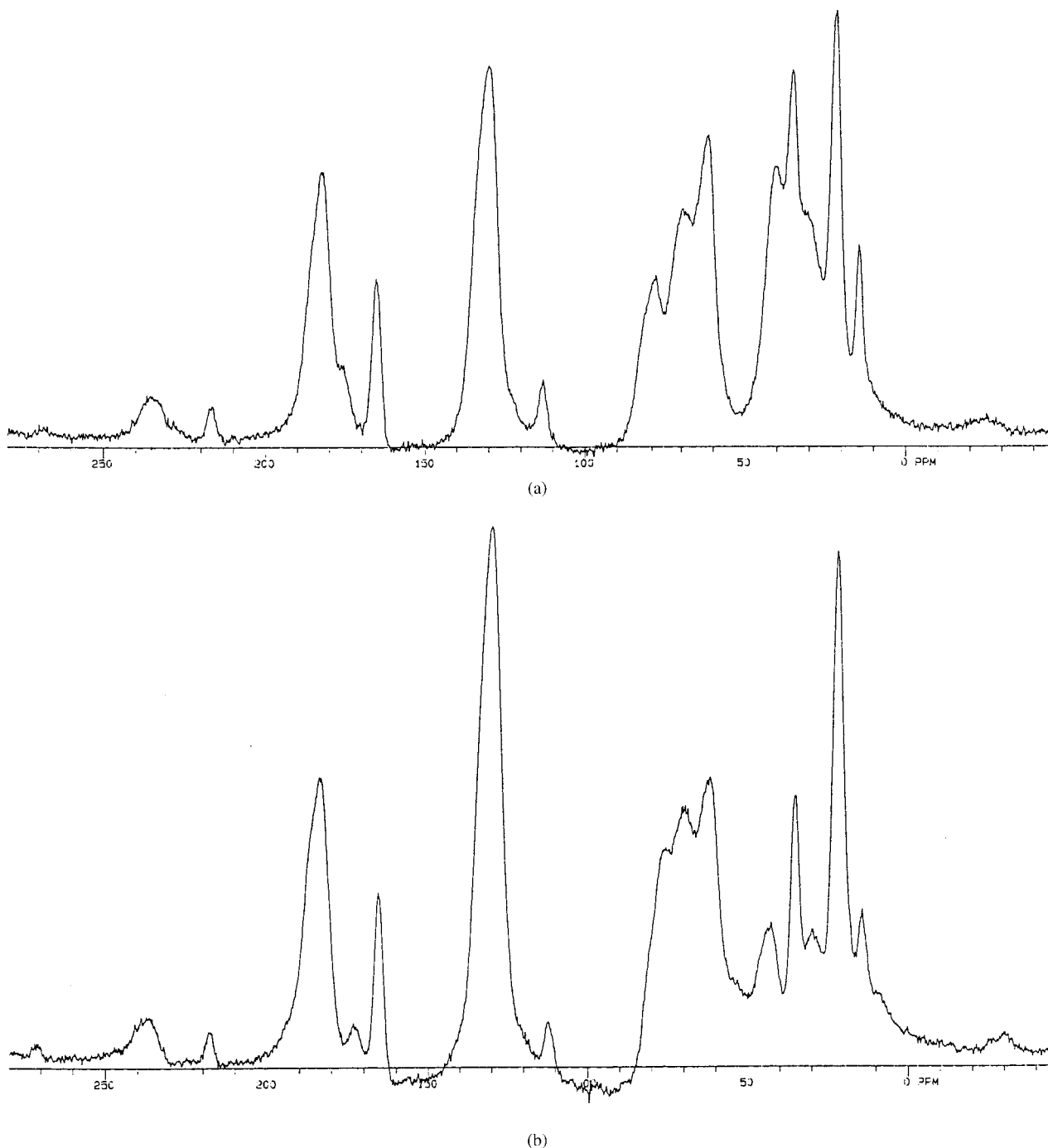
(a)

(b)

Figure 2   (a) NMR spectrum of P(EA-AA)-grafted polyester. (b) NMR spectrum of P(St-DEF-MAnh)-grafted polyester.

Figure 6. From the approximation, the raw polyester has 0.088 ms and 4.8 ms of $T_{1\rho H}$s.

The decay time distributions of P(EA-AA) and P(St-DEF-MAnh) were obtained by the similar procedure described above. Results are shown in Figures 7 and 8. The P(EA-AA) has 0.18 and 2.0 ms of $T_{1\rho H}$ and the P(St-DEF-MAnh) has 0.22 and 3.4 ms of that. These values were different from the values of the raw polyester.

First, we studied T_{1pH} of the P(EA-AA)-grafted polyesters. In a previous article,[14] we reported that the blend of the ungrafted polyester and the
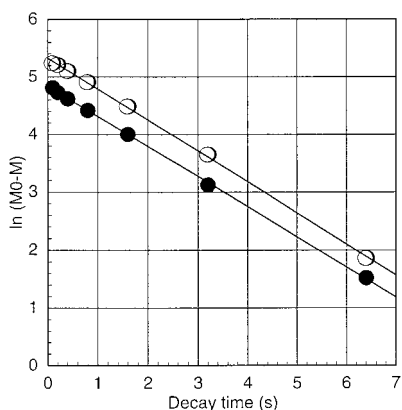
(a)
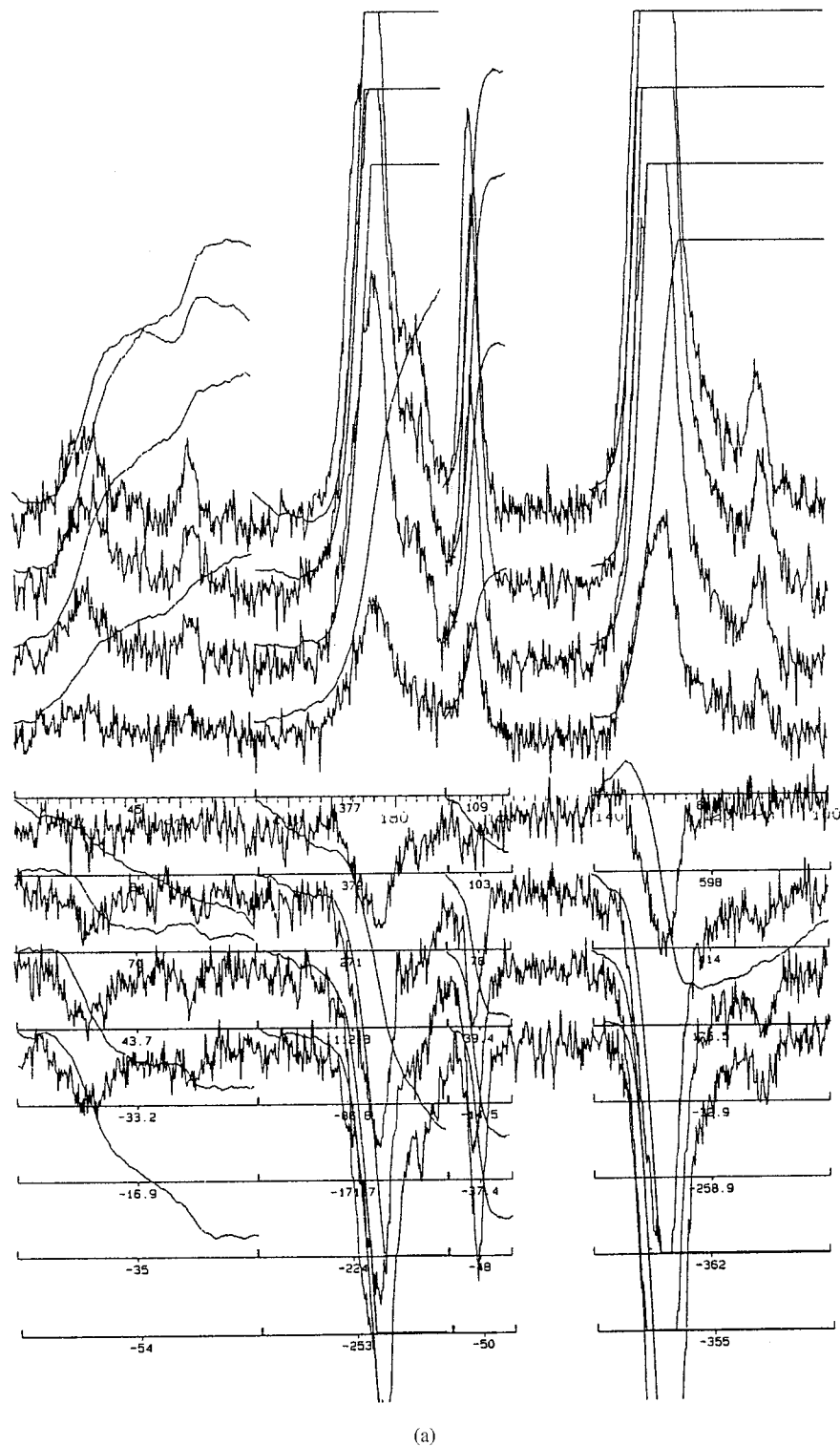
Figure 3   (a) Proton inversion-recovery crosspolarization measurements of the polyester segment of P(EA-AA)-grafted polyester. (b) Proton inversion-recovery crosspolarization measurements of the acrylics segment of P(EA-AA)-grafted polyester.

(b)
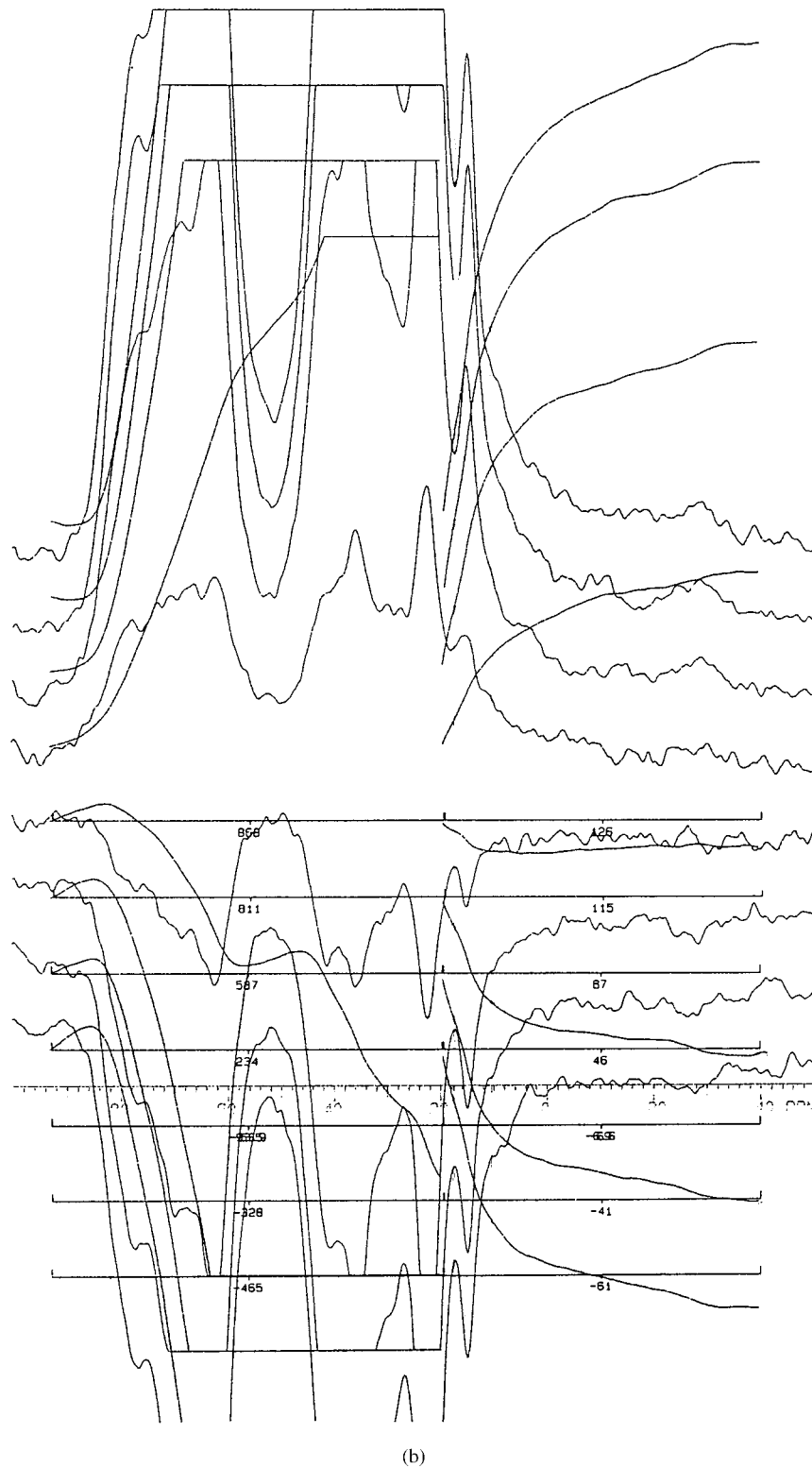
Figure 3 *(Continued)*
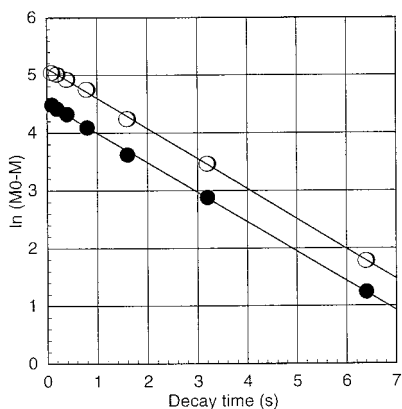
(a)

(b)

Figure 4 (a) Relationships between $M_0 - M(t)$ and the decay time for the P(EA-AA)-grafted polyester. ○: polyester (main chain). ●: P(EA-AA) (side chain). (b) Relationships between $M_0 - M(t)$ and the decay time for the P(St-DEF-MAnh)-grafted polyesters. ○: polyester (main chain). ●: P(EA-AA) (side chain).

P(EA-AA) was immiscible. Figure 9 shows the decay time distributions of the main chain and the side chain of the P(EA-AA)-grafted polyester,

Table III T_{1H} **Values for the Main Chains (Polyester Segment) and the Side Chains (Acrylics Segment) in the Grafted Polyesters**

	Main Chain (s)	Side Chain (s)
Polyester-*g*-P(EA-AA)[a]	1.93	1.97
Polyester-*g*-P(St-DEF-MAnh)[b]	1.85	1.85

[a] The mass ratio of polyester/ethyl acrylate (EA)/acrylic acid (AA) is 75/10/15.
[b] The mass ratio of polyester/styrene (St)/diethyl fumarate (DEF)/maleic anhydride (MAnh) is 75/10/10/5.
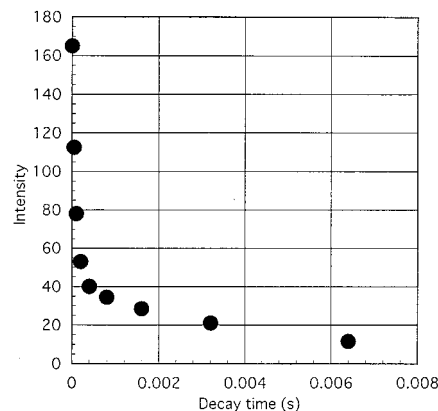

Figure 5 Relationship between the intensity and the decay time of the raw polyester.

respectively. From Figures 6 and 9, there was no change in $T_{1\rho H}$ or its distribution of the main chain before and after grafting. This result means that the main chain was immiscible with the side chain at the molecular level. From Figures 7 and 9, $T_{1\rho H}$ and its distribution of the side chain were slightly changed after grafting. This result seems valid because the side chain is attached to the main chain. As described above, from the value of t (~ 0.1 ms), T_2 (~ 10 μs) and l_0 (~ 0.1 nm), eq. (1) gives a value for the root-mean-square pathlength of 3 nm. This means that the size of the phase separation was at the nanometer level. From these results, it was found that the main chain and the side chain were immiscible at the molecular level.

Next, we studied $T_{1\rho H}$ of the P(St-DEF-MAnh)-grafted polyester. In a previous article,[14] we reported that the blend of the ungrafted polyester
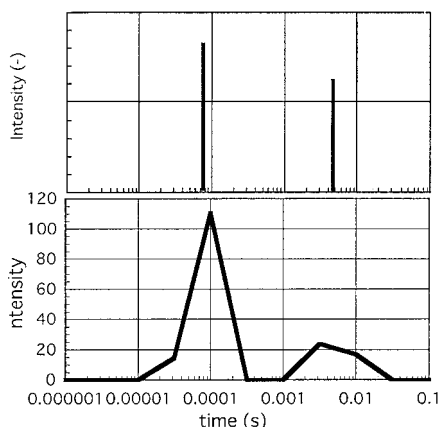

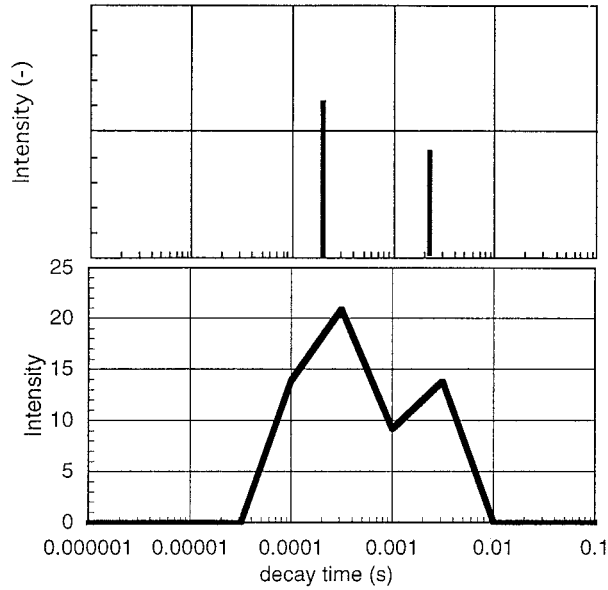**Figure 6** Decay time distribution of the raw polyester.

Figure 7 Decay time distribution of the P(EA-AA).

Figure 9 Decay time distributions of the P(EA-AA)-grafted polyester. (a) Polyester segment; (black line): (b); acrylics segment; (gray line).

and the P(St-DEF-MAnh) was miscible. Figure 10 shows the decay time distributions of the main chain and the side chain of P(St-DEF-MAnh)-grafted polyester, respectively. Compared with Figure 6, Figure 10 shows that $T_{1\rho H}$ and its distribution of the main chain were changed by the grafting of the P(St-DEF-MAnh). This result means that the main chain exists in a different environment from that before the grafting. In Fig-
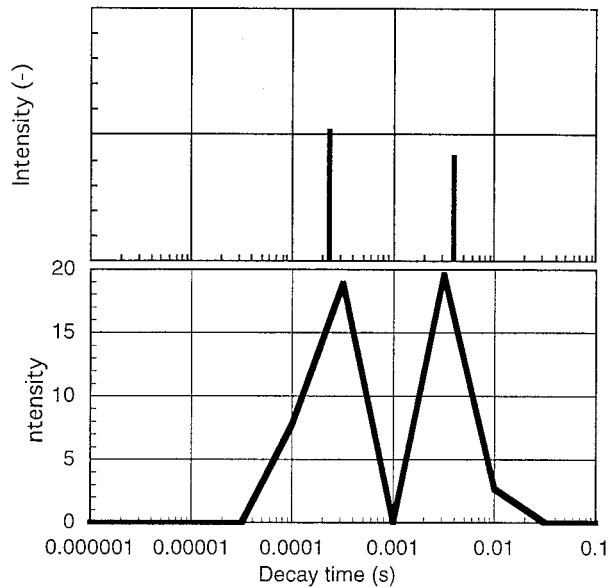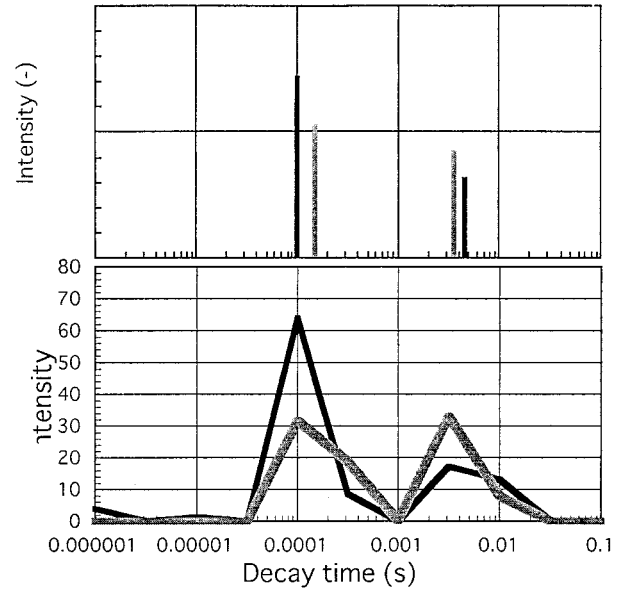
ures 8 and 10, $T_{1\rho H}$ and its distribution of the side chain were changed after grafting. $T_{1\rho H}$s and their distribution of the ungrafted polyester and the P(St-DEF-MAnh) were significantly different. From Figure 10, however, $T_{1\rho H}$s and their distribution of the main chain and the side chain were
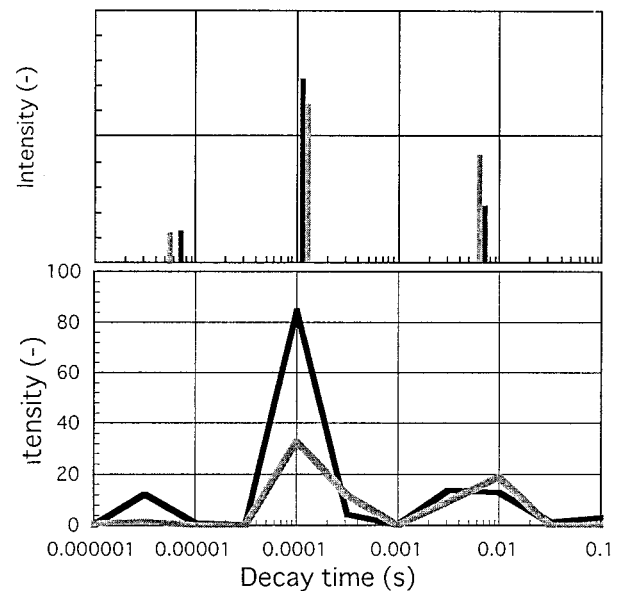

Figure 8 Decay time distribution of the P(St-DEF-MAnh).

Figure 10 Decay time distributions of the P(St-DEF-MAnh)-grafted polyester. (a) Polyester segment; (black line): (b); acrylics segment; (gray line).

similar. These results show that the main chain and the side chain of the grafted polyester exist in the same environment.

From the above results, it was found that the main chain (the polyester segment) and the side chain (the acrylic segment) were miscible at the molecular level. In grafted polymers, it was found that the compatibility of the main chain segment and the side chain segment effected the microstructures of the grafted polymers. From the results of the mechanical properties of two grafted polyesters, the difference in the microstructures effects the mechanical properties, i.e., tensile strengths, elongation to break, etc.

CONCLUSION

Structural study of two grafted polyesters, which were different in mechanical properties, was investigated by DMA, TEM, and solid-state ^{13}C-NMR. Using DMA and TEM, a separated phase larger than 100 nm was not found in the grafted polyesters. The main chain and the side chain appeared to be miscible in the grafted polyester. However, analysis of $T_{1\rho H}$s and their distributions made the difference of the microstructure in the grafted polyesters clear. P(EA-AA)-grafted polyester, which was very brittle, had a separated phase in the grafted polyester. The separated phase was estimated at about 3 nm. On the other hand, P(St-DEF-MAnh)-grafted polyester, which was very ductile, had a homogeneous microstructure. It appeared that the difference in the micro-structures of the grafted polyesters effected the mechanical properties of the grafted polyesters.

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