Molecular Motion and Properties of Flexible Fluoropolymers by ^1H Pulse NMR

Etsuko KATO^H,* Chikashi KAWASHIMA,* and Isao ANDO**

*Central Glass Co., Ltd., Tokyo Research Center,
2805 Imafuku-nakadai, Kawagoe, Saitama 350-11, Japan

**Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan

ABSTRACT: ^1H pulse NMR experiments are carried out for graft fluoropolymers with both flexibility and thermoplasticity over a wide range of temperatures, in order to elucidate exact dynamical feature in the solid state. From these experimental results, it was found that the graft fluoropolymers consist of a rubber-like (mobile) component and a crystalline (immobile) component in the solid state, and the graft fluoropolymer with different molecular weight of the base polymer being the rubber-like component has almost same ^1H T_2 value. These molecular motions clearly associate with mechanical properties.

KEY WORDS ^1H Pulse NMR / Spin-Spin Relaxation Time / ^1H T_2 / Solid Echo / Fluoropolymer / Graft Polymer / Molecular Motion /

Fluororubbers need complicated vulcanization processes to create their excellent properties. On the other hand, it is almost impossible for fluoropolymers with rigid thermoplastic property to improve those with soft thermoplastic property by only blending plasticizer. From this point of view, fluoropolymers with both properties of preferable flexibility and thermoplasticity have been developed. Most recently, we have reported that graft copolymers containing both the rubber-like component and crystalline component have high flexibility and tensile strength.¹

Physical properties of solid polymers are greatly influenced by the structure and the degree of molecular motion of the segmental units. It is very important to clarify the relationship between the molecular motion and properties of fluoropolymers. Until now, details of the structure and molecular motion of the polymers have been incompletely clarified.

On the other hand, it has been demonstrated that ^1H pulse NMR is a powerful tool for studying the dynamics of polymer.² For example, Jonas *et al.* have reported that ^1H

spin-spin relaxation times (T_2) of *cis*-1,4-polybutadiene are sensitive to slow motion and are affected by the presence of permanent chemical crosslinks or molecular entanglements.³ This shows that ^1H pulse NMR method is a powerful tool for elucidating molecular motion of polymers with branching.

From such a situation, the purpose of this work is to carry out ^1H pulse NMR experiments on fluoropolymers and to elucidate molecular motion associated with their structure.

EXPERIMENTAL

Materials

Fluoropolymers under consideration were prepared by the two step procedures.⁴ In the first step: Copolymer of vinylidene fluoride (VDF), chlorotrifluoroethylene (CTFE) and unsaturated peroxide (such as $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CO}-\text{O}-t\text{-Bu}$) was prepared at low temperature as follows.

Hereafter the copolymer is so-called 'base polymer'. By this reaction, base polymer could be obtained with some side chains $-\text{CH}_2-\text{O}-\text{CO}-\text{O}-t\text{-Bu}$. Base polymers with molecular weight of 5.6×10^4 and 2.6×10^4 were named base polymers H and L, respectively.

In the second step: The $\text{CH}_2-\text{O}-\text{CO}-\text{O}-t\text{-Bu}$ side chains are cleaved by raising the temperature. The free radicals produced initiate polymerization of VDF and flexible fluoropolymer as follows.

The obtained polymer by reaction of base polymer H and VDF was named graft polymer H and the obtained polymer by reaction of base polymer L and VDF was named graft polymer L.

The blend polymers H and L were obtained by a mixture of base polymer H and PVDF, and base polymer L and PVDF (Pennwalt KYNAR 710), respectively, at 180°C .

Measurements

^1H pulse NMR spectra were measured by means of a JEOL-Mu25 NMR spectrometer operating at 25 MHz in the temperature range of room temperature to 120°C . The pulse width was $2.0 \mu\text{s}$ and the number of accumulations was 32. For the ^1H T_2 measurements, the solid echo pulse sequence was used.⁵

The viscosity was determined by the flow tester viscometry (Shimazu Co., Ltd.) at 200°C .

The tensile strength was determined by the tensile test meter (Olientech Co., Ltd.) at room temperature.

RESULTS AND DISCUSSION

^1H pulse NMR of Fluoropolymers

PVDF homopolymer is crystalline, but the copolymer of VDF and CTFE becomes an elastomer. As the copolymer of VDF and CTFE (base polymer) has random structure, it is expected that consecutive VDF units exist in the chain. In Figure 1 is shown a typical ^1H T_2 curve of base polymer H at room temperature.

The fraction for these two components was (phases 1 and 2) obtained by the conventional procedure that longer T_2 was determined and then the remaining T_2 was determined by subtracting the long T_2 curve from the original T_2 curve. This T_2 curve consists of short T_2 and long T_2 decays which come from immobile (amorphous) and mobile (interfacial) components, respectively. The determined ^1H T_2 values are listed in Table I. The short T_2 decay can be assigned to the immobile component of consecutive VDF units (A) in base polymer, which are crystallized and, on the other hand, the long T_2 decay can be assigned to the mobile VDF units neighboring to the CTFE unit (B), which are not crystallized as indicated by

Figure 1. ^1H T_2 curve of base polymer H obtained by the solid echo method at room temperature.

Table I. ^1H T_2 of base polymer, graft polymer and PVDF as determined by the solid echo method at room temperature

	^1H $T_2/\mu\text{s}$		
	Phase 1 (Amorphous phase)	Phase 2 (Interfacial phase)	Phase 3 (Crystalline phase)
Base polymer	65	29	—
Graft polymer	108	33	15
PVDF	—	—	16

Figure 2. ^1H T_2 curve of graft polymer H obtained by the solid echo method at room temperature.

In Figure 2 is shown a typical ^1H T_2 curve of graft polymer H at room temperature.

This T_2 curve consists of three kinds of T_2 decays (phases 1, 2, and 3). The determined T_2 values of graft polymer H are listed in Table I, together with base polymer H and PVDF. The shortest T_2 (phases 3) decay is assigned to the crystalline component of VDF units. The remaining two T_2 decays correspond to the two T_2 decays of base polymer H.

The Effect of the Molecular Weight of Base Polymer on ^1H T_2

To elucidate the effect of the molecular weight of base polymer on ^1H T_2 , the ^1H T_2 experiments were carried out as a function of temperature. In Figure 3 are shown tempera-

Figure 3. Temperature dependences of ^1H T_2 (a) and fraction (b) for individual components of base polymer. Solid line, base polymer H; broken line, base polymer L.

ture dependences of ^1H T_2 of base polymers L and H (a) and the fraction of each component for T_2 decay of them (b).

There is no difference in ^1H T_2 between base polymers L and H in the temperature range of 20 to 120°C. On the other hand, there is clear difference in the fraction of each component for ^1H T_2 decay between base polymers H and L above 80°C, but no difference below 80°C. At high temperatures, the fraction of the immobile component in base polymer H is larger compared with the case of base polymer L. From the above results, it was shown that the molecular motion of the base polymer is restrained with an increase of molecular weight.

In Figure 4 are shown temperature dependences of ^1H T_2 value of graft polymers L and H (a) and the fraction of each component of T_2 decays of them (b).

There are no difference in ^1H T_2 and the fraction of each component of ^1H T_2 decay in this temperature range of 20 to 120°C. How-

Figure 4. Temperature dependences of ^1H T_2 (a) and fraction (b) for individual components of graft polymer. Solid line, graft polymer H; broken line, graft polymer L.

ever, there is a large difference in the case of the base polymer. From the above results, it was found that the molecular motion of graft polymers is independent of the molecular weight of its base polymer.

A Comparison of the Molecular Motion of Graft Polymer and Blend Polymer

In Figure 5 are shown temperature dependences of ^1H T_2 of base polymer H and graft polymer H.

It is shown that the molecular motion of graft polymer H is more restrained than that of base polymer H at high temperatures. The shortest ^1H T_2 value in graft polymer H is independent of temperature within experimental errors. Therefore, it can be said that the shortest ^1H T_2 decay comes from PVDF homopolymer contained in the graft polymer.

In order to clarify the existence of PVDF homopolymer contained in the graft polymer,

Figure 5. Temperature dependences of ^1H T_2 for base polymer and graft polymer. Solid line, base polymer H; broken line, graft polymer H.

Figure 6. Temperature dependences of ^1H T_2 for base polymer, blend polymer and graft polymer. Solid line, base polymer H; broken line, graft polymer H and semi-broken line, blend polymer H.

molecular motion of graft polymer, and a blend of PVDF and base polymer was compared with each other in detail. In Figure 6 are shown temperature dependences of ^1H T_2 of base polymer H, graft polymer H and blend polymer H.

It was shown that ^1H T_2 plots against temperature for blend polymer H are between those for base polymer H and graft polymer H. From the above results, it was found that the molecular motion for a blend of base polymer and PVDF is more restrained than that for the base polymer but is faster than the graft polymer.

On the basis of the above experimental results, it is suggested that the model scheme for the structure of fluoropolymer is shown in Figure 7.

Figures 7(a) and (b) show model schemes

Figure 7. The scheme for the structure of fluoropolymer.

for graft polymers H and L, respectively. On the other hand, Figures (c) and (d) shows model scheme for graft polymers H and L, respectively, when these polymers are stretched. These model schemes show that the amount of the entanglement between the base polymer chains is gradually increased with an increase of their molecular weights. Nevertheless, their molecular motions are very close to each other. This means that the molecular motion of the base polymer chains is strongly affected by the crystallites of the graft chains.

Molecular Motion and Properties of Fluoropolymers

Table II shows typical properties of base polymer, blend polymer, and graft polymer. Base polymer L has high flow rate but has weak tensile strength and low elongation ratio. On the other hand, base polymer H has low flow rate, large tensile strength and high elongation ratio. From the above experiments, it is ex-

Table II. Mechanical properties of fluoropolymers

Sample	Physical properties			
	flow rate $\times 10^{-3}$ ml s^{-1} (200°C)	Viscosity $\times 10^4$ poise (200°C)	Tensile strength	Tensile rate
			MPa	%
Base polymer L	1.3	19	7	418
Base polymer H	0.2	120	17	599
Blend polymer L	6.0	4	14	181
Blend polymer H	0.9	27	26	460
Graft polymer L	5.8	4	30	563
Graft polymer H	4.7	5	28	520

pected that the difference in mechanical properties between base polymers H and L comes from the difference in their molecular motion as is seen from the experimental finding that the fraction of the immobile components for the base polymer H is larger than that for sample base polymer L. However, graft polymers L and H have almost the same mechani-

cal properties. From ^1H T_2 experimental results, it is apparent that the graft polymers H and L are undergoing almost the same molecular motion.

From the above results, it can be concluded that these molecular motions clearly associate with mechanical properties.

REFERENCES

1. C. Kawashima and T. Koga, *Plastics*, **39**, 98 (1988).
2. a) A. Abragam, "Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961; b) D. W. McCall, "Molecular Dynamics and Structure," R. S. Carter and J. J. Rush, Ed., NBS, Special Publication 301, Washington D.C., 1969, p. 475; c) T. C. Farrar, E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N.Y., 1971; d) V. J. McBrierty, "Comprehensive Polymer Science," C. Booth and C. Price, Ed., Pergamon Press, London, 1989, p. 397; e) J. Mathias, Ed., "Solid State NMR of Polymers," Plenum Press, New York, N. Y., 1991.
3. G. C. Munie and J. Jonas, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1061 (1980).
4. a) M. Hada and K. Aoshima, *Finechemical*, **11**, 5 (1985); b) T. Kawashima, Jpn. Patent Syo 59—30847.
5. a) J. G. Powles and J. H. Strange, *Proc. Phys. Soc.*, **6**, 82 (1963); b) P. Mansfield, *Phys. Rev.*, **A961**, 137 (1965).