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Molecular Motion of ABA Block Copolymer in mixed Solvent by NMR and ESR

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混合溶媒中の ABA 型ブロック コーポリマーの分子運動

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概 要

近年、高分子化学研究においてはブロックコーポリマーの溶液物性が注目されており、 $^1\text{H-NMR}$ 法および粘度法などが、ブロックコーポリマーの分子運動を解析する手段として、これまでもちいられてきた。最近になり、ポリオキエチレン-ポリスチレン系の AB 型ブロックコーポリマーの分子運動が混合溶媒中で研究され、溶媒との相互作用に大きく左右されることが示されている。それは、ハイドロホービックブロックが溶媒和により液相として存在する場合には、相当した NMR 吸収ピークが明確に観測され、さらに温度依存性も示されるというものである。

当研究では、2種の重合度の異なったポリオキシエチレン-ポリオキシプロピレン-ポリオキシエチレンの ABA 型ブロックポリマーをもちい、ベンゼン-ジオキサンおよび水-ジオキサンの混合溶媒中でのブロックコーポリマーの分子運動を調べた。測定手段としては $^1\text{H-NMR}$ 法および ESR 法をもちいた。

その結果、重合度比が 100 : 40 : 100 の NP-68 サンプルの NMR は、ベンゼン-ジオキサン混合溶媒のベンゼン比が増加するにしたがい、末端の OH 基の半値巾が減少することが観測された。これは ESR の最大傾斜巾の傾向ともよく一致する。一方、両端のポリオキシエチレンの重合度の低い NP-64 サンプル（重合度比が 20 : 40 : 20）では、混合溶媒の組成をかえても OH 基の半値巾の変化はほとんど観測されなかった。しかし、この NP-64 サンプルを水-ジオキサン混合溶媒中で調べると、CH 基の半値巾がそれぞれ

の単一溶媒の場合に比較して大きく拡がっていることがわかった。これらのことから、ABA型コポリマーは溶媒中で単一ポリマーのような1つの分子としての挙動をするのではなく、溶媒の種類および組成によって、コポリマーのとりうる分子形態も変化することが示された。

Molecular Motion of ABA Block Copolymer in mixed Solvent by NMR and ESR

It is known that polyoxypropylene become hydrophobic in molecular weight above 900. The nonionic surface active agent containing polyoxypropylene (plronics) is prepared by the addition of ethylene oxide to polyoxypropylene. Recently, molecular motion of block copolymer in solution has been investigated by NMR spectra and intrinsic viscosity etc.¹⁾, Nakamura et al studied molecular motion of each block of polyoxyethylene-polystyrene and plronics²⁾. They reported that resonances of the hydrophobic block in mixed solvent could be observed if they exist as liquid phase, and also that molecular motion of hydrophobic block of copolymers were activated not only by interaction with solvent but also by an increase in temperature.

We will study to obtain the further information about the plronics molecular motion using NMR and ESR. ESR method is suitable to study of system having slow correlation times. In the case of NMR method, we will be able to obtain information not only CH proton peak but also OH proton peak.

Experimental

Samples from Sanyo Kasei were available. Average number molecular weight of polymers were 8000 (NP-68) and 3000 (NP-64). These samples were tri-block type copolymer which consisted of polyoxyethylene block, polyoxypropylene block and polyoxyethylene block. Averaged degrees of polymerization of each other block for samples were 100:40:100 for NP-68, and 20:40:20 for NP-64.

¹H-NMR spectra were obtained at 100 MHz using a JNM-FX 100 spectrometer. Samples were contained in 5 mm OD glass tube and were degassed. The solvents, benzene-d₆, dioxane-d₈ and water-d₂ were obtained from E. Merck. The polymer concentration was 5 mg / 0.1 ml. Tetramethylsilane was added to each solution as external reference, measurements were made at 5-80 °C. ESR spectra were obtained using a JEOL FE 3 X spectrometer utilizing 100 KHz field modulation at 5-80 °C. Polymer samples were spin-labeled by the dehydrating the terminal OH with 2, 2, 5, 5-tetramethyl 1-pyrrolidinyloxy 3-carboxylic acid.

Result and Discussion

Initially, we examined that intermolecular association exist or not, because the NP-68 and NP-64 polymers were the surface active agent. Surface tension of NP-68 or NP-64 polymer was measured at 25 °C. Each curve of surface tension did not have CMC point. From this result, these polymers do not form intermolecular association. Result of VPO measurement also supported this conclusion. Fig 1 shows NMR spectra of OH proton of NP-68 polymer in mixed solvent at various solvent composition³⁾. The OH proton resonance peak is broadened in mixed solvent (benzene/dioxane). On the other hand, when the composition ratios are 7/3 and 1/1 (benzene/dioxane), proton peaks are sharp. From this result in mixed solvent, the shapes of spectra are largely dependent on solvent composition.

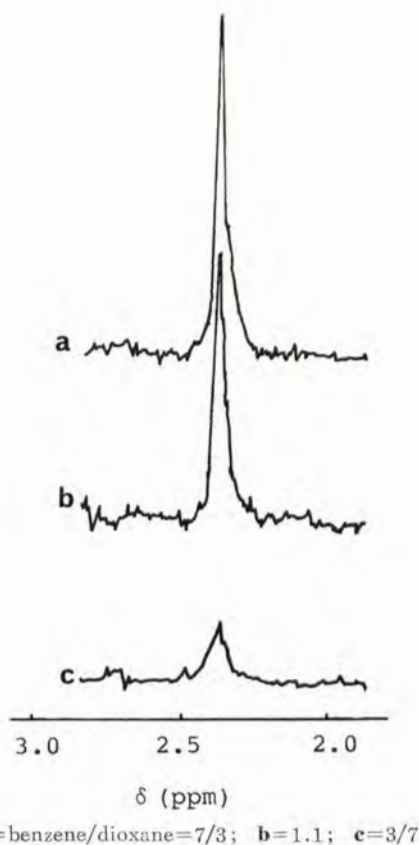


Fig. 1 100 MHz ^1H -NMR Spectra of OH Proton of NP-68 at 41 °C as a Function of Solvent Composition.

We conclude that the molecular motion of polyoxyethylene block of NP-68 polymer in mixed solvent are affected by interaction with good solvent (benzene)⁴, because the degree of polymerization of polyoxyethylene block is much larger than that of polyoxypropylene. Polyoxypropylene block is contracted in comparison with polyoxyethylene block in benzene. Therefore, this does not affect to mobility of polyoxyethylene block.

An analysis was necessary that mobility of OH group reflect the molecular motion of whole molecular of polyoxyethylene block or not, because the OH group was especial group in polymer. Therefore the spin-labeled polymer at OH groups in solution were measured by ESR. Fig 2 shows maximum slope width center field line, corresponding to $M_1 = 0$ for NP-68 labeled polymer in benzene + dioxane as a function of solvent composition. For the region of motionally narrowed line shape, 10^{-9} to 10^{-11} s, the correlation times (τ_c) were calculated by the equation.

$$\tau_c = C \Delta W_{msl} [(h_0/h_{-1})^{1/2} - (h_0/h_{+1})^{1/2}]$$

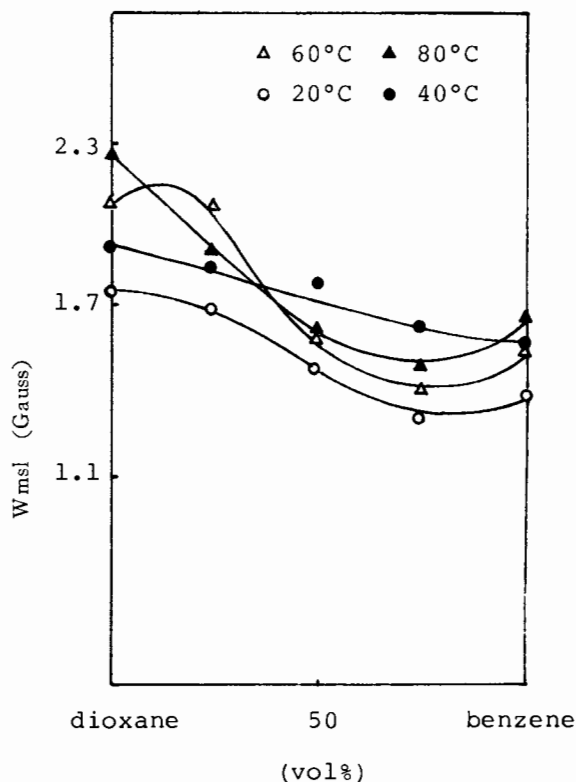


Fig. 2 Maximum Slope widths of Center Field Line, Corresponding to $M_1 = 0$, for NP-68 and Labeled Polymer as a Function of Solvent Composition.

Here, ΔW_{msl} is maximum slope width of the center field line, and h_0 , h_{-1} , and h_{+1} are the signal heights of high, center, and low field lines. The constant c is a parameter depending on the anisotropics of the hyperfine interaction and the g -factor. The value of maximum slope width decreases as an increase in volume ratio of benzene in mixed solvent. This result of ESR measurement agree well with that of NMR measurement.

Consequently, the mobility of OH group reflect that of whole molecular of polyoxyethylene block in copolymer. Fig. 3 shows maximum slope widths for NP-68 labeled polymer as a function of solvent composition in water + dioxane. The degree of decrease for maximum slope width is larger than that. From this result, polyoxyethylene block expand in water comparison with benzene, interaction between polymer and water is stronger than between polymer and benzene. On the other hand, the NMR spectra observed for the OH proton of the NP-64 polymer as a function of solvent composition at 40°C are shown in Fig 4. The shape of OH

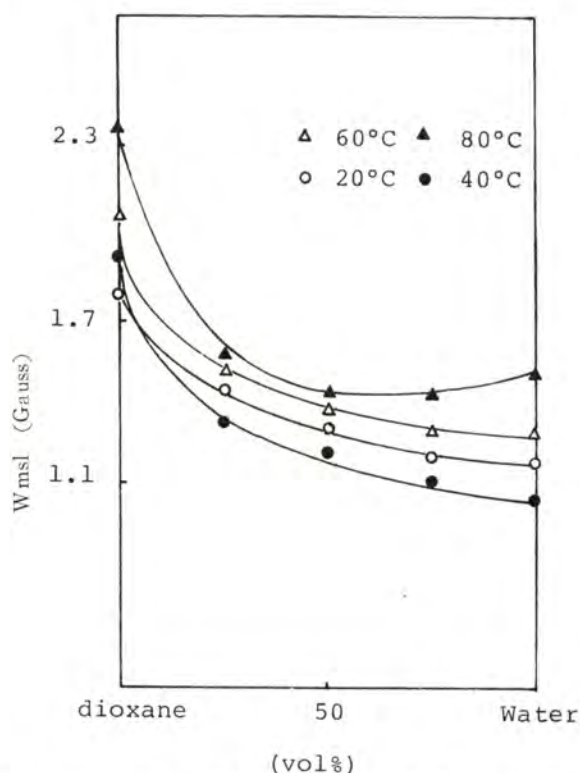


Fig. 3 Maximum Slope Widths of Center Field Line. Corresponding to $M_1 = 0$, for NP-68 Labeled Polymer as Function of Solvent Composition.

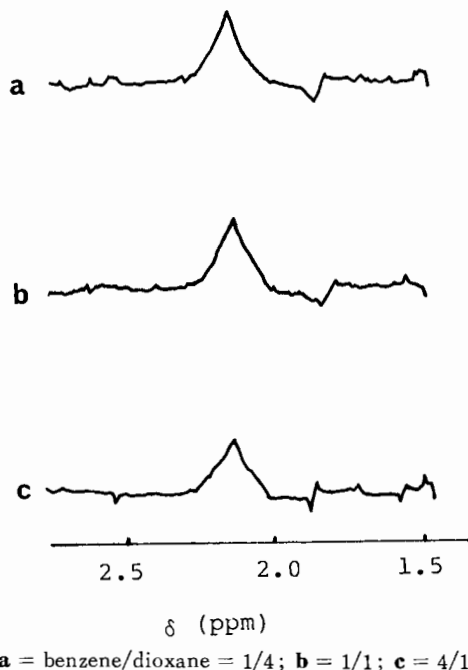


Fig. 4 100 MHz ^1H -NMR Spectra of OH Proton of NP-64 at 41 °C as a Function of Solvent Composition.

proton peak is almost independent of solvent composition. From the results of NP-64 polymer in mixed solvent benzene- d_6 + dioxane- d_6 , it is suggested that the molecular motion of polyoxyethylene block is independent of solvent composition.

It can be presumed that polyoxypropylene block affect to mobility of polyoxyethylene block. The mobility of polyoxyethylene is interpreted reasonably as follows, polyoxypropylene chain do not so expand, even if ratio of volume of benzene in mixed solvent is increased. Benzene is good solvent for polyoxyethylene, so the polymer chain is expected to expand as the ratio is increased. But degree of expansion of NP-64 polymer molecule is small by reason that polyoxyethylene block is not so long, and molecular motion of polyoxypropylene block which is slowly than that of polyoxyethylene block affected to mobility of OH group by reason that polyoxyethylene block is not so long. Mobility of OH group in NP-64 polymer is influenced by not only the expansion of polyoxyethylene block but also expansion of polyoxypropylene block.

Fig 5 shows the NMR spectra observed for the CH proton in polyoxypropylene block of the NP-64 polymer in mixed solvent (water/dioxane) at 41 °C. The CH resonance proton is almost dependent of solvent composition. In Fig 5, the spectra

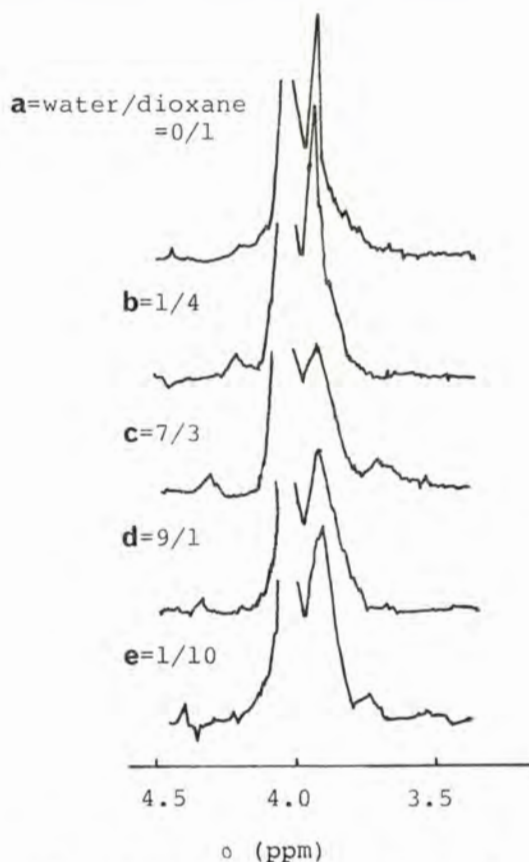


Fig. 5 100 MHz ^1H -NMR Spectra of Methine Proton of NP-64 at 40°C as a Function of Solvent Composition.

of CH for (a) and (b) are sharp, these solution contained little volume of water. The spectra of (c), (d) and (e) are broad comparison with those of (a) and (b). The shape of the peak of CH proton in NP-64 polymer is dependent on solvent composition and temperature. From the results of NP-64 polymer in mixed solvent water- d_2 +dioxane- d_8 ⁵⁾, it is suggested that the molecular motion of polyoxypropylene block is dependent on solvent composition; water is good solvent for polyoxyethylene and poor solvent for polyoxypropylene, dioxane is good for polyoxypropylene but no good for polyoxyethylene. Therefore, polyoxypropylene block is almost expand in dioxane, but the degree of expansion decrease as increase in volume ratio of water in mixed solvent. The expansion of NP-64 becomes minimum when the solvent composition of water/dioxane is 7/3. When the composition of water increases, polyoxyethylene block becomes to expand due to the interaction between water and

polymer. From the facts presented above, the contracted polyoxypropylene block is a little relaxed by the expanded polyoxyethylene block. But this effect is small by reason that the ethylene block is not so long. In the result of intrinsic viscosity measurement, the value of $[\eta]$ at water/dioxane = 7/3 was maximum.^{6,7)} This fact supports the previous explanation. After all, the mobility of propylene block in NP-64 polymer is affected by expansion of polyoxyethylene block, because polyoxypropylene chain is short.

Fig. 6 shows temperature and solvent composition dependence of volume of chemical shift for OH proton resonance for NP-68 polymer in mixed solvent (dioxane/benzene). The value of chemical shift is expressed in ppm with respect to the tetramethylsilane. The only resonance of OH peak in pure benzene-d₆ shift to higher field, but the values of chemical shift for OH proton do not vary with the solvent composition. This result can be explained that the OH groups are hydrogen-bonded with the oxygen atoms of the dioxane molecule. Whatever composition of solvent change, the H-bond remain largely. The tendency which the resonance of

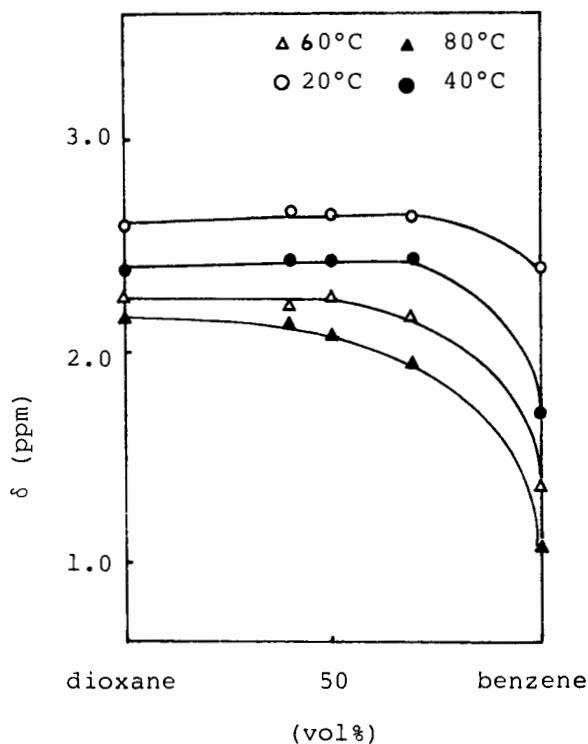


Fig. 6 Temperature and Solvent Composition Dependence of The Chemical Shift for OH Proton in NP-68.

OH peak in pure benzen-d₆ shift to higher field due to ring current shielding effect of benzene ring. Variaton of chemical shift in mixed solvent as temperature raised may be attribute to decomposition of hydrogen-bond.

References

- 1) J.P. Home and S. Bywater, *Macromolecules*, **4**, 544 (1971).
- 2) K. Nakamura, R. Endo and M. Takeda, *J. Polym. Sci.*, **15**, 2095 (1977).
- 3) V.D. Mochel, T.W. Bethea and S. Futamura, *Polymer*, **20**, 65 (1979).
- 4) C. Rossi and V. Magnasco, *J. Polym. Sci.*, **58**, 977 (1962).
- 5) G.N. Malcolm and J.S. Rowlinson, *J.S. Trans. Faraday Soc.*, **53**, 921 (1957).
- 6) L. Gargallo, D. Radic and I. Katime, *Eur. Polym. J.*, **16**, 383 (1980).
- 7) C. Sadron and R. Rempp, *J. Polym. Sci.*, **29**, 127 (1958).