A Study of Solvent Exchange Process in (Ethylene–Vinyl Alcohol) Copolymer Gels by a Proton Nuclear Magnetic Resonance Spectroscopy Imaging Method

Masahito Kanekiyo,[1] Masatoshi Kobayashi,[1] Isao Ando,[1] Hiromichi Kurosu,[2] Shigetoshi Amiya[3]

[1]*Department of Chemistry and Materials Science, International Research Center of Macromolecular Science, Tokyo Institute of Technology, Ōokayama, Meguro-ku, Tokyo, Japan*
[2]*Department of Human Life and Environment, Nara Women's University, Kitauoya-Nishimachi, Nara, Japan*
[3]*Analytical Research Center, Kuraray Company, Ltd., Kurashiki, Okayama, Japan*

ABSTRACT: The proton nuclear magnetic resonance (^{1}H NMR) image patterns of (ethylene–vinyl alcohol) copolymer (EVOH)/dimethylsulfoxide (DMSO) gels with various ethylene contents were measured to elucidate the process of solvent exchange between DMSO and water in the gels soaked in water. The results of these experiments indicate that the rate of solvent exchange between DMSO and water in the gels increased with an increase in the ethylene content of EVOH copolymers. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 504–508, 2002

Key words: ethylene–vinyl alcohol copolymer; gel; network polymer; solvent exchange; ^{1}H NMR imaging

INTRODUCTION

It is known that poly(vinyl alcohol) (PVA) in aqueous solution,[1] in dimethylsulfoxide (DMSO) solution,[2] and in water/DMSO mixtures[3–5] forms gel by undergoing freeze–thaw cycles that lead to formation of hydrogen bonds between the PVA interchains.[1] From high-resolution solid-state ^{13}C NMR experiments on PVA gels,[6,7] it has been elucidated that there exist two kinds of regions in the gel with different molecular motion, and that the CH carbon signal in the slow motion region splits into three peaks like solid PVA.[8,9] The latter peaks come from the CH carbon with two hydrogen bonds, one hydrogen bond, and no hydrogen bond. Furthermore, in addition to these studies, the structure and dynamics of PVA gel system have been elucidated in detail by ^{1}H pulse NMR, high-resolution solid-state ^{13}C NMR, and dynamic viscoelasticity methods.[10–12]

In previous works, on the basis of knowledge of the structure and dynamics of (ethylene–vinyl alcohol) copolymer (EVOH) in the solution state[13] and in the solid state,[14–16] the structure and dynamics of solid EVOH[14] and EVOH gel[17] copolymers with a wide range of ethylene contents have been studied by high-resolution solid-state ^{13}C NMR. It has been shown that the copolymers are mainly composed of two kinds of regions with relatively fast and slow molecular mo-

tions that come from the mobile and immobile regions, respectively. Furthermore, from the solid-state ^{13}C NMR experimental results, it was found that the formation of hydrogen bonds between the hydroxyl groups in the vinyl alcohol parts of EVOH copolymers with high vinyl alcohol fraction and the formation of hydrophobic interactions between the methylene groups in the CH_2 parts of EVOH copolymers with high ethylene fraction contribute to its gel formation. Also, EVOH forms a gel when dissolving in a mixture of DMSO and H_2O. However, EVOH cannot form in water by undergoing freeze–thaw cycles because only a small amount of EVOH is dissolved. This phenomenon may be due to difference between DMSO–EVOH network and H_2O–EVOH network intermolecular interactions. It is very important to clarify intermolecular interactions between solvents and the polymer network. ^{1}H NMR imaging experiments in real time are expected to be useful as a method for approaching this problem.

In previous studies,[18–21] to clarify changes of macroscopic structure and dynamics of water molecules in a polymer gel by the application of an external stimulus, such as stress and electric field, by observation of microscopic information at the molecular level, the ^{1}H NMR imaging patterns with information about the spatial distribution of the ^{1}H spin density and the ^{1}H spin–spin relaxation time T_2 of water molecules in the polymer gel have been measured. From these experimental results, it has been demonstrated that ^{1}H NMR imaging is a useful means for elucidating the stress–strain process and the shrinkage process by the appli-
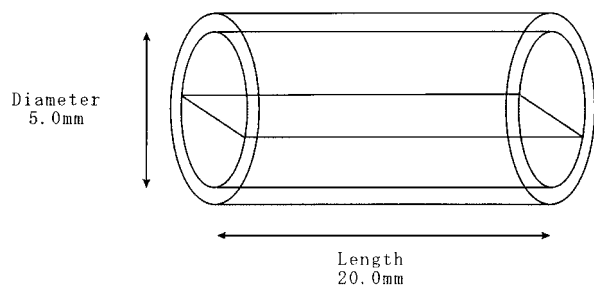
Figure 1 A diagram of a transverse slice section of a gel with a diameter of 5 mm and a length of 20 mm to be observed by ^{1}H NMR imaging.

cation of an electric field to a polymer gel, as well as ^{1}H NMR imaging works in polymer materials.[22–25]

In this study, from such a background, we aim to elucidate three-dimensionally the solvent exchange process between DMSO and H_2O in EVOH gels by the ^{1}H NMR imaging experiments in real time.

EXPERIMENTAL SECTION

Materials

EVOH copolymers with ethylene contents of 5% [EVOH(5%)] and 48% [EVOH(48%)] were used in this work and were obtained from Kuraray Company Ltd. The microstructure of these EVOH copolymers was already characterized by solution ^{13}C NMR and reported previously.[13]

The gel was prepared from EVOH/dimethylsulfoxide (DMSO) or deuterated DMSO(d-DMSO) solution by repeating the freeze–thaw cycle (freezing at $-20\,^\circ$C for 20 h and then melting at $20\,^\circ$C for 4 h) three times. The EVOH gel sample was prepared in a cylindrical Teflon tube with a diameter of 5.0 mm, as shown in Figure 1.

Measurements

The ^{1}H NMR imaging measurements were carried out with a JEOL GSX-270 NMR spectrometer operating at 270 MHz and equipped with a JEOL NM-GIM270 imaging system at 296K. In these experiments, the ^{1}H spin density and the ^{1}H T_2 weighted images of water molecules in the gel were observed. As reported previously,[18–21] this imaging pulse sequence is based on the spin–echo pulse sequence of Hahn.[26] The data processing for a two-dimensional image pattern were performed by the Fourier imaging method. In the ^{1}H NMR imaging experiments, the gradient strengths used for the slice selection, phase-encoding, and readout are 220, 220, and 220 mT/m, respectively, and the slice thickness is 1.0 mm.

The gel sample was placed at the middle of a cylindrical sealed glass cell that was filled with saturated H_2O or D_2O solution to analyze solvent exchange between two kinds of DMSO in the gel and water or D_2O solvents placed on the top of the gel, as shown in Figure 2. DMSO in the EVOH/DMSO gels was exchanged by D_2O, and d-DMSO in EVOH/d-DMSO gels were exchanged by H_2O. Some ^{1}H NMR image patterns of composite EVOH gels were measured as a function of the elapsed time after the addition of H_2O or D_2O solution. The images obtained were analyzed with a GXDIMG image analysis system(LSIC Company Ltd.) to get a profile of the ^{1}H spin density images.

RESULTS AND DISCUSSION

If an EVOH(48%)/DMSO gel disk with the diameter of 30 mm and thickness of 2 mm was placed in water, the gel was promptly shrunk and was changed from a transparent state to a nebulous state. At the elapsed time (T_e) of 24 h, it became a disk with a diameter of 25 mm. On the other hand, when an EVOH(5%)/DMSO disk with the diameter of 30 mm was placed in water, the gel was extremely changed within the elapsed time. At $T_e = 24$ h, it became a disk with the diameter of 29 mm. At $T_e = 168$ h, it became a disk with the diameter of 27 mm. It still was transparent.

The ^{1}H spin density images of an EVOH/DMSO gel (DMSO) are measured, as shown in Figure 3, where the magnitude of the ^{1}H spin density is differentiated by 256 steps between the lowest and highest spin densities and then observed ^{1}H spin density image is represented by colors from black, representing the lowest density, to white, representing the highest density. The intensity scale indicated by colors is shown in
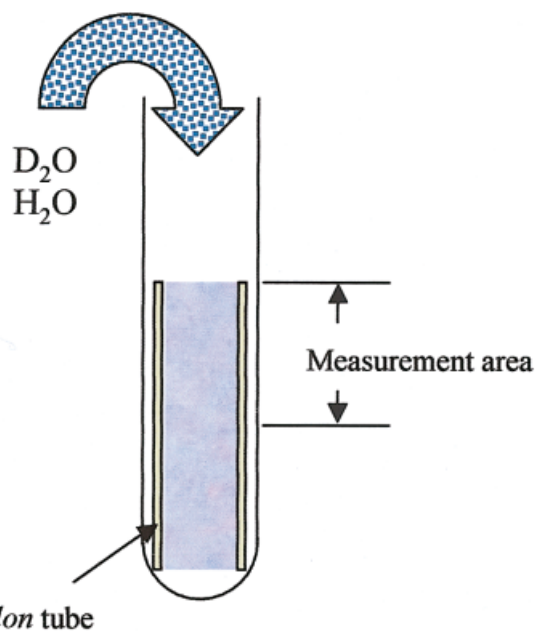

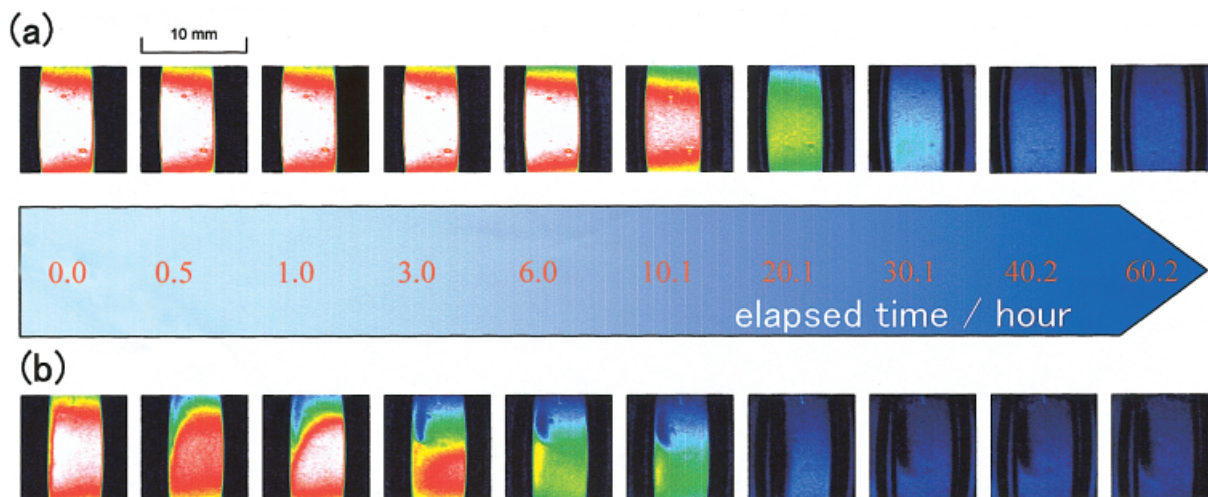**Figure 2** A diagram of a gel sample placed in a Teflon tube.

Figure 3 The elapsed-time dependence of ^{1}H NMR images for the ^{1}H spin density of an EVOH/DMSO gel with an addition of D_2O. In EVOH copolymers, (a) ethylene content = 5% and (b) ethylene content = 48%.

Figure 4, where the color scale indicates the relative value of the ^{1}H spin density.

In the solvent exchange process of a EVOH(5%)/DMSO gel placed in D_2O, it is expected that DMSO solvent gets out from the gel within the elapsed time. The ^{1}H spin density image begins to change from the top of the gel with the elapsed time as seen from the image changes: white→red→orange→yellow→olive green→light blue→blue (Figure 3a). At T_e = 0 h the cross-section area of the gel is occupied as a whole by the white region, corresponding to a high ^{1}H spin density area. At T_e = 6 h ,the cross-section area of the gel is occupied as a whole by the white region, which is the high ^{1}H spin density region. At T_e = 10.1 h, the ^{1}H spin density changes as indicated by white→red→orange→yellow→olive green. After T_e = 20.1 h, the olive green and light blue regions corresponding to the intermediate ^{1}H spin density region expand. At T_e = 60.2 h, the whole region is occupied

by the blue region, corresponding to the low ^{1}H spin density region.

On the other hand, in the solvent exchange process of a EVOH(48%)/DMSO gel placed in D_2O, the image of the ^{1}H spin density begins to change from the top of the gel with the elapsed time, as seen from the following image changes: white→red→orange→yellow→olive green→light blue→blue (Figure 3b). It is shown that at T_e = 0 h, the image is occupied as a whole by the white region corresponding to the high ^{1}H spin density region. At T_e = 3 h, more than half of the whole image is occupied by the red region, corresponding to the high ^{1}H spin density region. At T_e = 6 h, the image is occupied as a whole by the olive green region, corresponding to the low ^{1}H spin density region. At T_e = 20.1 h, the whole region is occupied by the blue region, corresponding to the low ^{1}H spin density area. From these experimental results, it is seen that at 20.1 h, the blue region from both of the right and left sides of the low ^{1}H spin density image comes from changes of DMSO signal. Thus, it can be said that the DMSO solvent comes out from the inside of the gel to the outside.

It is seen from Figure 5 that the intensity of the ^{1}H spin density of the solvent in EVOH gel of ethylene content 48 % decreased more quickly than that of the EVOH gel of ethylene content 5 %. This result is because the difference in penetration speed of the outside solvent into a gel between an EVOH gel of ethylene content 48 % and an EVOH gel of ethylene content 5 % is very large (Figure 8, shown below).

The ^{1}H spin density image for an EVOH(48%)/d-DMSO gel is indicated in Figure 6. In the solvent exchange process between d-DMSO and H_2O in the EVOH gel, the ^{1}H spin density image changes from the top to the low ^{1}H spin density regions with the elapsed time as light blue→olive green→yellow→orange→red. At T_e

Figure 4 The intensity scale indicates by the relative value of the ^{1}H spin density with colors.
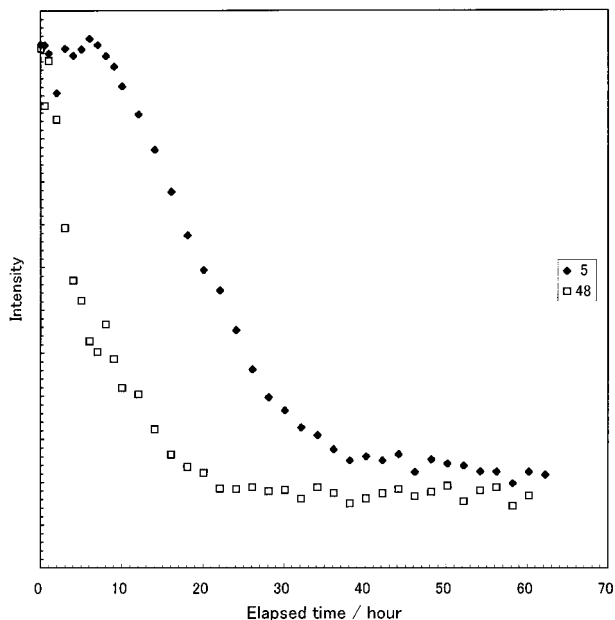
Figure 5 Intensity of the ^{1}H spin density image of DMSO solvent in an EVOH gel against the elapsed time at a depth of 5 mm from the surface of a gel. In EVOH copolymers, ♦: ethylene content = 5% and □: ethylene content = 48%.
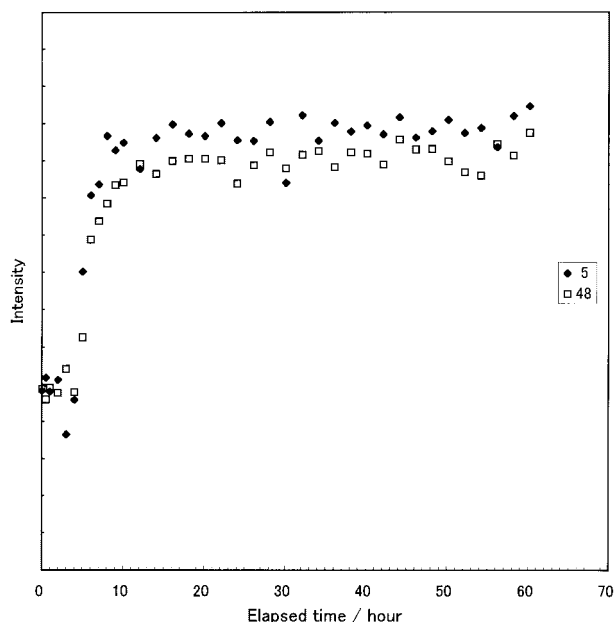
Figure 7 Intensity of the ^{1}H spin density of H_2O solvent in an EVOH gel against the elapsed time at depth of 5 mm from the cylindrical surface of the gel. In EVOH copolymers, ♦: ethylene content = 5% and □: ethylene content = 48%.

= 0 h, most of the image is occupied by the light blue region, corresponding to the low ^{1}H spin density area. And, at T_e = 6 h, the image is changed as yellow→olive green region, corresponding to the intermediate ^{1}H spin density region. At T_e = 60.2 h, the red region corresponding to the high ^{1}H spin density region is increased. Thus, it can be said that the increase of the high ^{1}H spin density region corresponding to the white and the red regions on both the right and left sides of the image comes from penetration of H_2O solvent from the outside of the gel. From the ^{1}H spin density images of EVOH(5%) and EVOH(48%) gels as a function of the

elapsed time, the rates of increase of the high ^{1}H spin density region corresponding to the red region of the image for these gels are almost same (Figure 7).

To clarify the solvent exchange process between d-DMSO and H_2O in the EVOH gels, we measure the penetration time of H_2O from the outside of the gel to the inside by ^{1}H NMR imaging. The plots of the penetration depth d of H_2O placed on the top of a cylindrical gel as measured by ^{1}H NMR imaging against the elapsed time t are shown in Figure 8. From the mean-squares fits, we obtained the following equation:
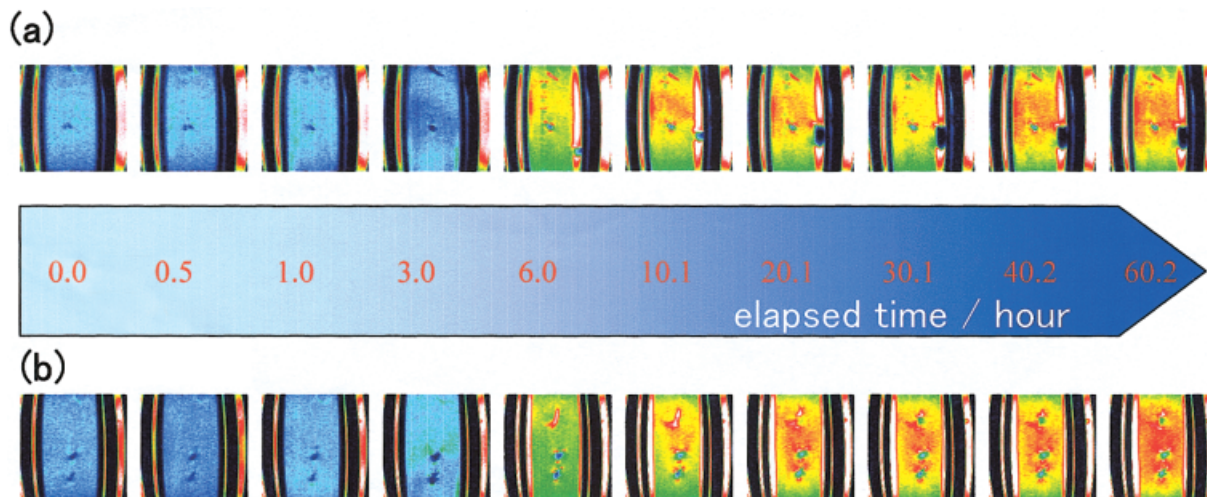

Figure 6 The elapsed time dependence of the ^{1}H spin density image of a EVOH/d-DMSO gel with the addition of H_2O. In EVOH copolymers, (a) ethylene content = 5% and (b) ethylene content = 48%
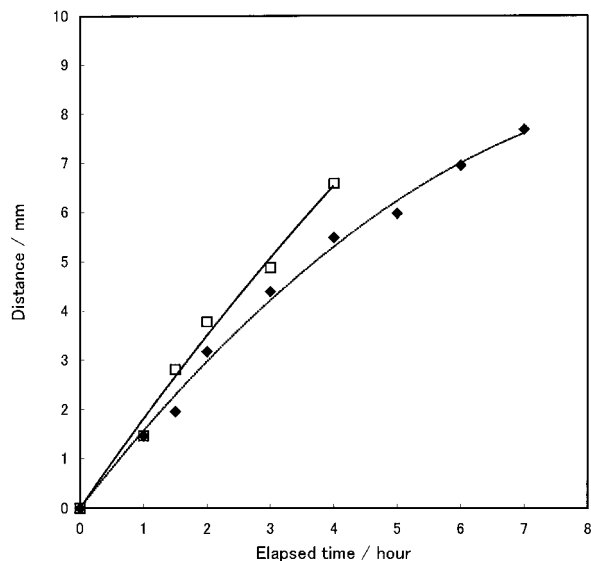
Figure 8   Arrived depth profile of D_2O solvent in an EVOH gel against the elapsed time In EVOH copolymers, ♦: ethylene content = 5% and □: ethylene content = 48%.

$$d = -at^2 + b$$

where for EVOH(5%) gel, the values of a and b are 0.0798 and 1.65, respectively, and for EVOH(48%) gel, these values are 0.0575 and 1.87, respectively.

From these experimental results on EVOH(5%) and EVOH(48%) gels, it is seen that the penetration speed of water through EVOH(48%) gel is much faster than that through EVOH(5%) gel. This result may be because the network of EVOH(48%) has strong hydrophobic interaction and weak hydrophilic interaction compared with EVOH(5%) gel, and the affinity of the network and DMSO in the gel is weak.

Finally, from these experimental results, we conclude the following: The rate of solvent exchange between DMSO and water in the gels increases with an increase in the ethylene content of EVOH copolymers. Furthermore, the NMR imaging method is a useful means for elucidating the solvent exchange process in gels.

References

1. Takahashi, A.; Hiramatsu, S. Polym J 1974, 6, 103.
2. Rogozhin, S.V.; Losinsky, V.J.; Vainerman, E.S.; Domotenko, L.V.; Mamtsis, A.M.; Ivanova S.A., et al. Dokl Akad Nauk USSR 1984, 278, 129.
3. Yamaura, K.; Itoh M.; Matsuzawa S. J Appl Polym Sci 1989. 37, 2709.
4. Cha, W.-I.; Hyon, S.-H.; Ikada, Y. Makromol. Chem 1992, 193, 13.
5. Ohkura, M.; Kanaya T.; Kaji. K. Polymer 1992, 33, 3686.
6. Kobayashi, M.; Ando, I.; Ishii, T.; Amiya, S. Macromolecules 1995, 28, 6677.
7. Kobayashi, M.; Ando, I.; Ishii, T.; Amiya, S. J. Mol Struct 1998, 440, 155.
8. Terao, T.; Maeda, S.; Saika, A. Macromolecules 1983, 16, 1535.
9. Horii, F.; Hu, S.; Ito, T.; Odani, H.; Kitamura R. Polymer 1992, 33, 2299.
10. Kanekiyo, M.; Kobayashi, M.; Kurosu, H.; Ando, I.; Ishii, T.; Amiya, S. J Mol Struct 1998, 447, 49.
11. Kobayashi, M.; Kanekiyo, M.; Ando, I. Polym Gels Networks 1998, 6, 347.
12. Kobayashi, M.; Kanekiyo, M.; Ando, I.; Amiya, S. Polym Gels Networks 1998, 6, 425.
13. Ketels, H.; Beulen, J.; Velden, G. Macromolecules 1988, 21, 2032.
14. Kanekiyo, M.; Kobayashi, M.; Ando, I.; Kurosu, H.; Amiya, S. Polymer 2000, 41, 2391.
15. Ketels, H.; Haan, J. de.; Aerdts, A.; Velden, G. Polymer 1990, 31, 1419.
16. VanderHart, D. L.; Simmons, S.; Gilman, J. W. Polymer 1995, 36, 4223.
17. Kanekiyo, M.; Kobayashi, M.; Ando, I.; Kurosu, H.; Amiya, S. Macromolecules 2000, 33, 7971.
18. Yasunaga, H.; Kurosu, H.; Ando, I. Macromolecules 1992, 25, 6505.
19. Shibuya, T.; Yasunaga, H.; Kurosu, H.; Ando, I. Macromolecules 1995, 28, 4377.
20. Kurosu, H.; Shibuya, T.; Yasunaga, H.; Ando, I. Polym J 1996, 28, 80.
21. Yamazaki, A.; Hotta, Y.; Kurosu, H.; Ando, I. Polymer 1998, 39, 1511.
22. Listerud, J. M.; Sinton, S. W.; Drobny, G. P. Anal Chem 1989, 61, 23A.
23. Weisenberger L. A.; Koenig, J. L. Macromolecules 1990, 23, 2445.
24. Weisenberger L. A.; Koenig, J. L. Macromolecules 1990, 23, 2454
25. Grinsted R. A.; Koenig, J. L. Macromolecules 1992, 25, 1229.
26 Hahn, E. L. Phys Rev 1950, 80, 580.