

DMS AND ^{13}C NMR STUDIES ON THE COMPATIBILITY AND DYNAMICS OF LATEX BIDIRECTIONAL IPNS AND LATEX IPN OF PVAc/PBA

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ABSTRACT

The compatibility and dynamics of latex bidirectional interpenetrating polymer networks (LBIPNs) and latex IPN (LIPN) of poly(vinyl acetate) (PVAc) and poly(butyl acrylate) (PBA) are investigated by means of dynamic mechanical spectroscopy (DMS) and nuclear magnetic resonance (NMR) techniques. The results of DMS show that the compatibility of the LBIPNs is much better than that of the corresponding LIPN and depends to a large extent on the distribution of PVAc both in the core and in the shell. The results of NMR measurements indicate that the rotational correlation times of the side-groups of PBA in the LBIPN are longer than those in the LIPN. The relation between the ^{13}C linewidths of PBA and temperature is also discussed.

INTRODUCTION

The properties of polymer-polymer blends depend to a large extent on their synergistic effect, which is determined by their miscibility or compatibility. A polymer blend of two components 1 and 2 is miscible thermodynamically if the Gibbs free energy of mixing $\Delta G < 0$ and $[\partial^2 G / \partial^2 \phi_2]_{T, P} > 0$. But most polymer pairs are thermodynamically immiscible due to $\Delta G > 0$. It can be, therefore, said that improving polymer-polymer miscibility or compatibility is one of the most important research areas on polymer blends or polymer alloys.

Interpenetrating Polymer Networks (i. e. IPNs) are the new category of polymer blends developed since the end of 1960s^[1, 2] and have the excellent properties^[3] because the interpenetration between the two networks (in fact, among the phase interfacial regions^[4]) leads to improve the compatibility and restrict the phase separation. Among all sorts of IPNs, Latex IPNs (i. e. LIPNs) have been widely used as damping materials^[5, 6] owing to their better compatibility, producibility and applicability. Although LIPNs can result in the improvement of compatibility, the majority of polymers, as stated above, is mutually immiscible, LIPN technique is not very efficient for the two components whose difference of solubility parameters are considerably large. In order to solve this problem, the method of latex bidirectional interpenetration is presented here. By this method, the networks of component 1 both in the core and in the shell interpenetrate with the network of component 2 in the intermediate layer, and it

can be achieved by seeded emulsion polymerization technique.

Many physical means have been used to characterize the miscibility or compatibility and dynamics of polymer blends. Now the compatibility of latex bidirectional interpenetrating polymer networks (i. e. LBIPNs) and the corresponding LIPN of poly(vinyl acetate) (PVAc) and poly(butyl acrylate) (PBA) is investigated by dynamic mechanical spectroscopy (DMS), and the information on the dynamics is obtained from ^{13}C spin-lattice relaxation times (T_1) and linewidths.

EXPERIMENTAL

1. Materials

Vinyl acetate (VAc) is distilled under vacuum to remove the inhibitor. Butyl acrylate (BA) is washed with 5% NaOH solution to remove the inhibitor. Divinyl benzene (DVB), sodium lauryl sulfate (SLS) and ammonium persulfate are used as received.

2. Preparation of Samples

The latexes of PVAc/PBA (1/1, weight ratio) LIPN and a series of PVAc/PBA/PVAc LBIPNs are prepared by two-step emulsion polymerization and three-step emulsion polymerization respectively. In detail, for the LIPN, the polymerization are carried out in a 500-ml three-necked flask immersed in a constant temperature bath at 343K and equipped with a reflux condenser, a stirrer and a 100-ml dropping funnel. Deionized water and emulsifier (SLS) are initially charged and mixed by stirring, following by an approximate addition of a half of the total ammonium persulfate initiator (dissolved in deionized water). The monomer of VAc containing 0.4% DVB is added through the dropping funnel at a rate of 2 ml/min. After about 1.5hrs, the rest of the initiator is added and then the monomer of BA containing 0.4% DVB is added through the funnel at the same rate, the latexes of the PVAc/PBA LIPN are obtained after 1.5hrs. For the LBIPNs, on the basis of the latexes of LIPNs prepared by the same way as above, the initiator is added and the monomer of VAc containing 0.4% DVB is added by dropping, the latexes of the LBIPNs are finally obtained after about 2hrs. The prepared latexes of the LIPN and LBIPNs are filmed and dried at 323K.

3. DMS measurements

The dynamic mechanical spectra of all samples are recorded on a DDV-III-EA dynamic viscoelastometer using 35Hz of frequency and 3 K/min of elevating temperature rate.

4. NMR measurements

The film samples of the LIPN and 0.5/1/0.5 (weight ratio) PVAc/PBA/PVAc LBIPN are rolled and then inserted into a 10mm-tube respectively, ^{13}C T_1 values at different temperatures are obtained by inversion-recovery method on a Bruker MSL-400 spectrometer operating at 100.63MHz for ^{13}C with 15.2 μs of 90°

pulse width, and the linewidths of the carbons in the film samples are measured from their normal ^{13}C spectra. The piece samples of the LIPN are randomly placed into a 10-mm tube, the linewidths of the carbons are also obtained from the normal ^{13}C spectrum.

RESULT AND DISCUSSION

Figure 1 shows the dynamic mechanical spectra of PVAc/PBA/PVAc

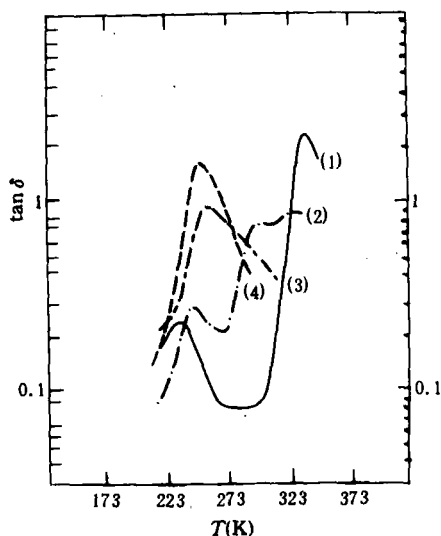
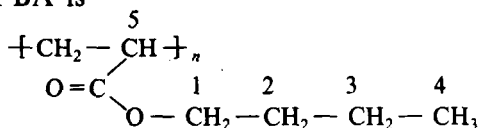


Fig.1 The damping factors ($\tan\delta$) of PVAc/PBA/PVAc LBIPNs and the corresponding LIPN as a function of temperature

- (1) 1/1 LIPN, (2) 0.25/1/0.75 LBIPN, (3) 0.41/1/0.59 LBIPN and (4) 0.5/1/0.5 LBIPN.

LBIPNs and the corresponding LIPN with the same composition as the LBIPNs. The LIPN has two individual damping peaks between which the damping factor is very small. This means that the two components are mutually incompatible. But the two peaks of the LBIPNs are mutually closed and even merged into a single, which obviously depends on the distribution of PVAc both in the core and in the shell. For instance, only a broadened damping peak is observed for both 0.5/1/0.5 and 0.41/1/0.59 PVAc/PBA/PVAc LBIPNs, which means that the two components are compatible. These results indicate that the LBIPN technique is an efficient means for improving compatibility of polymer blends especially the polymer blends composed of two immiscible components. Why the compatibility of LBIPNs is considerably better than that of the corresponding LIPN? This may be understood from the following three aspects: From the viewpoint of probability, the distribution of PVAc both in the core and in the shell can increase the interpenetrating probability. From the viewpoint of thermodynamics, LBIPNs have two transition regions, but LIPN has only one, because the transition region benefits compatibility of two components. In addition, the thermodynamic potential due to the strong interaction between PVAc and water compels the PVAc in the core to migrate outward and gives rise to the efficient mixing with PBA in the procedure of synthesis.

The ^{13}C resonance signals of the PVAc in IPNs can not usually be observed at the room temperature with the normal liquid probe because of its higher T_g , but the ^{13}C signals of the PBA in IPNs are observable. Hence the ^{13}C spin relaxation data of the PBA in IPNs can be determined with the normal liquid probe. The relations between the ^{13}C T_1 values of the PBA in the LIPN and the 0.5/1/0.5 PVAc/PBA/PVAc LBIPN are shown in Figure 2(a) and (b) respectively. The structure of PBA is



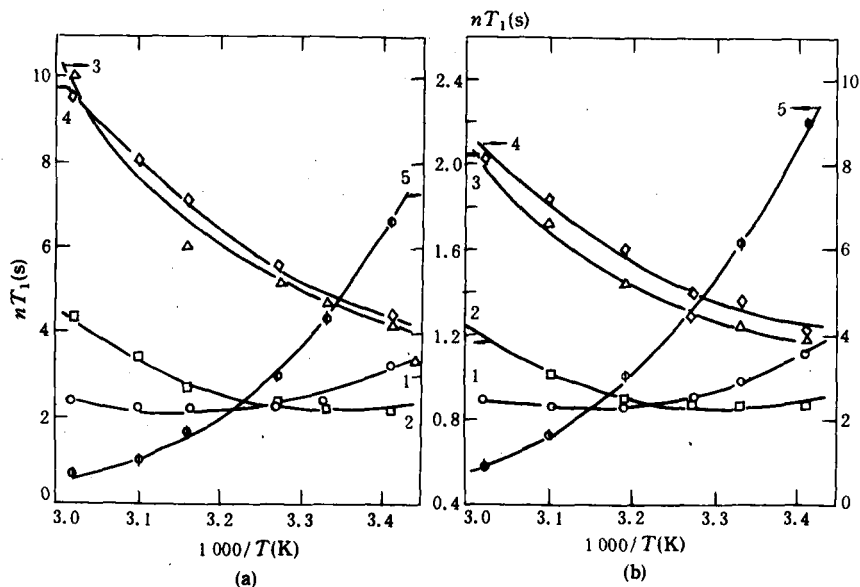


Fig.2 The ^{13}C spin-lattice relaxation times (nT_1) of the PBA in the LIPN (a) and the 0.5/1/0.5 LBIPN (b) as a function of temperature

It can be seen from Figure 2 that (1) the carbon 2, 3 and 4 (or propyl, ethyl and methyl) are in the region of the rapid motion i.e. $\omega\tau < 1$ where ω indicates the resonant angle frequency and τ represents the motional correlation time, (2) the carbon 1 (or butyl) approaches the region of the minimum value (that is $\omega\tau = 1$), and (3) the carbon 5 (or main chain) locates in the region of the slow motion i.e. $\omega\tau > 1$. Quantitatively, the ^{13}C T_1 due to the contribution of dipolar interaction can be expressed as ^[8]

$$1/T_1 = 0.1N\gamma_C^2\gamma_H^2\hbar^2 r^{-6} [J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (1)$$

where γ represents the magnetogyric ratio, $\hbar$ is the Planck constant divided by 2π , N represents the number of the protons attached to a carbon atom, r indicates the length of a C—H vector, and $J(\omega)$ is the spectral density function, which is the Fourier transform of the auto-correlation function $G(t)$ of the orientational motion of the C—H vector

$$J(\omega) = \int_{-\infty}^{+\infty} G(t) e^{-i\omega t} dt \quad (2)$$

The contribution to the ^{13}C spin relaxation of the side-groups in PBA due to the segmental motion is negligible in comparison with the contribution due to the self-rotation of the side-groups. Hence the correlation function of the i th internal rotation can be expressed as

$$G(t) = \sum_{a, b, \dots, i} [d_{ab}^{(2)}(\Delta_1)]^2 [d_{bc}^{(2)}(\Delta_2)]^2 \dots [d_{Ni}^{(2)}(\Delta_N)]^2 \\ [d_{i0}^{(2)}(\Delta_i)]^2 [\delta_{aa} + (1 - \delta_{aa})e^{-t/\tau_1}] [\delta_{bb} + (1 - \delta_{bb})e^{-t/\tau_2}] \\ \dots [\delta_{NN} + (1 - \delta_{NN})e^{-t/\tau_N}] [\delta_{ii} + (1 - \delta_{ii})e^{-t/\tau_i}] \quad (3)$$

in which $d^{[2]}$ indicates the reduced second-order Wigner rotational matrix, Δ_i represents the angle between a rotational axis and a C—H vector, and τ_i is the correlation time of the rotation. The correlation times of the side-groups of the PBA in the LIPN and LBIPN can be obtained from the experimental T_1 values based on the equations 1, 2 and 3. The results are listed in Table 1. These results show that the correlation times of the side-groups in the LBIPN are longer than those in the LIPN. As well known, efficient mixing between PBA and PVAc can cause the free volume of the PBA to decrease (i.e. the rate of motion to decrease). Therefore, these results indirectly illustrate that the compatibility of the LBIPN is better, which is consistent with the results of DMS. It can be also seen from Figure 2 that the T_1 values of the carbon 1 and 2 are insensitive to the variation in temperature while the T_1 values of the carbon 3 and 4 are sensitive in the range of measured temperature. Hence the rotational activation energy of the carbon 3 and 4 can be obtained from the correlation times at different temperatures based on Arrhenius equation

$$\tau = \tau_{\infty} e^{E_a/RT} \quad (4)$$

The values are 20.2 KJ/mol and 18.3KJ/mol for the carbon 3 in the LIPN and LBIPN respectively, and 19.7KJ/mol and 16.8KJ/mol for the carbon 4 in the LIPN and LBIPN respectively.

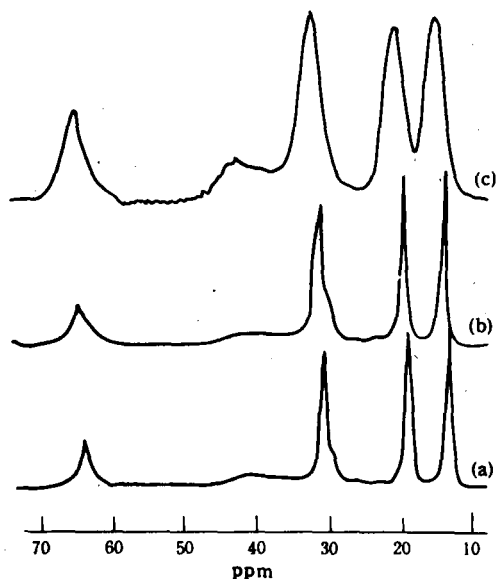


Fig.3 The ^{13}C NMR spectra of (a) the film sample of the LIPN, (b) the film sample of 0.5/1/0.5 PVAc/PBA/PVAc LBIPN, and (c) the piece sample of the LIPN at 296K

Figure 3 shows the ^{13}C spectra of (a) the film sample of the LIPN, (b) the film sample of 0.5/1/0.5 PVAc/PBA/PVAc LBIPN, and (c) the piece sample of the LIPN. The linewidths in (c) are much wider than those in (a), this indicates that the piece sample of the LIPN has considerably larger inhomogeneity in the static magnetic field and variations in bulk magnetic susceptibility. The linewidths in (b) are also broader than those in (a), this means that the motional narrowing of the LIPN is much efficient, which is consistent with the results discussed above.

The plots of $\text{Ln}(\text{Linewidth})$ [i.e. $\text{Ln}(\text{LW})$] vs. the reciprocal of Kelvin temperature are shown in Figure 4 (a), (b) and (c) which correspond to the three cases in Figure 3. No straight lines are obtained, this demonstrates that the variation in linewidths as temperature is inconsistent with Arrhenius equation. All plots of $-1/\log [\text{LW}(T)/\text{LW}(T_s)]$ vs. $1/(T-T_s)$ are shown in Figure 5. For the film samples of the LIPN and LBIPN, a roughly straight line and a fairly straight line are obtained respectively [see Figure 5 (a) and (b)]. These results show that WLF equation is available. But for the piece sample of the

Table 1 The rotational correlation times of the side-groups of the PBA in the LIPN and LBIPN (0.5/1/0.5) at different temperatures

No.	1 ($\tau \times 10^8$ s)		2 ($\tau \times 10^{10}$ s)		3 ($\tau \times 10^{11}$ s)		4 ($\tau \times 10^{11}$ s)	
Temp (K)	LIPN	LBIPN	LIPN	LBIPN	LIPN	LBIPN	LIPN	LBIPN
293	1.84	1.94	1.19	1.21	10.1	11.4	2.26	2.28
300	1.52	1.7	1.17	1.12	9.1	10.6	2.07	1.83
306	1.49	1.57	1.11	1.12	8.58	9.83	1.56	1.83
313	1.5	1.5	1.03	1.08	7.02	8.28	1.09	1.38
323	1.47	1.52	0.845	0.928	5.38	6.73	1.08	1.13
331	1.51	1.53	0.713	0.747	4.4	5.35	0.929	1.11

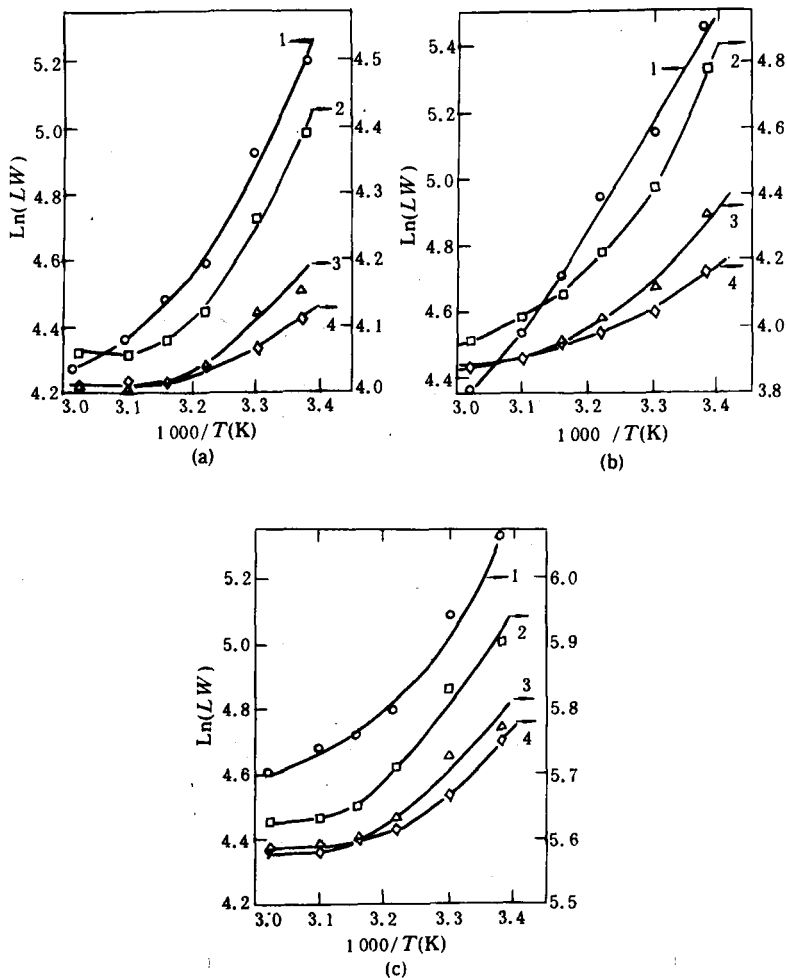


Fig.4 The plots of $\text{Ln}(LW)$ vs. the reciprocal of temperatures (a), (b) and (c) correspond to the three cases stated in Figure 3

LIPN , no straight lines are obtained [see Figure 5 (c)] , this means that WLF equation is unsuitable. In polymers above T_g , the major line-broadening mechanisms for ^{13}C can be usually separated into those that produce a distribution of resonance frequencies and those that arise from relaxation process^[7]. The

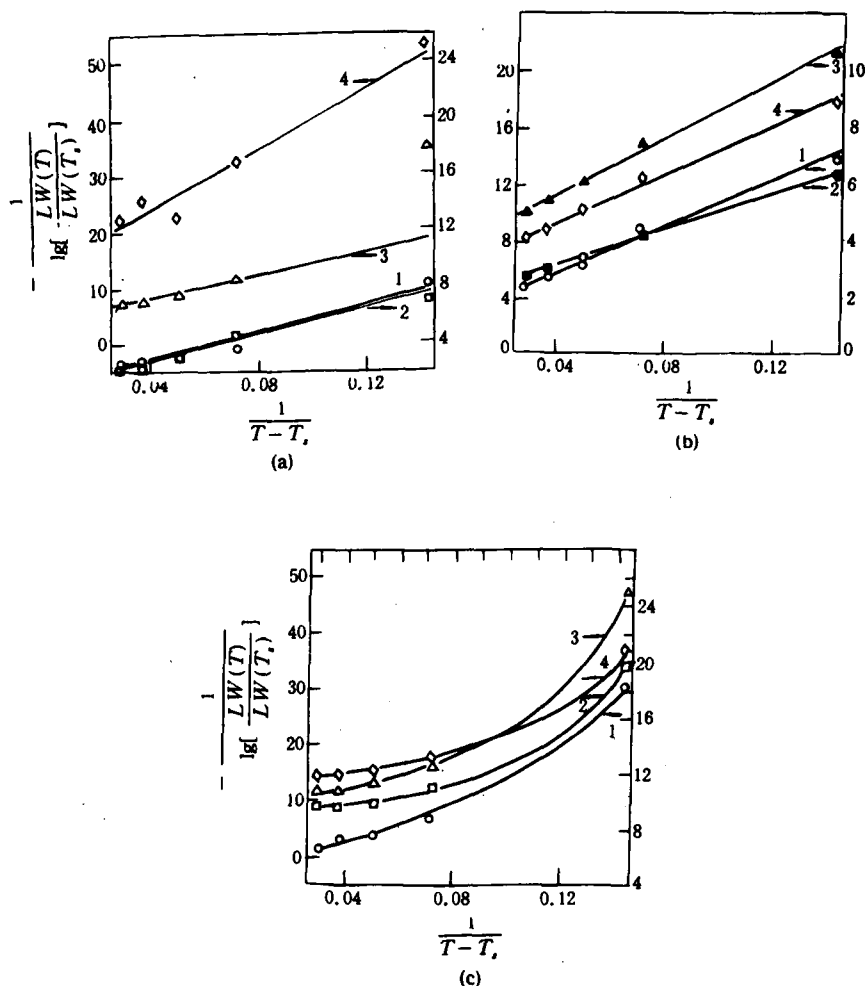


Fig.5 The plots of $-1/\lg [LW(T)/LW(T_s)]$ vs. $1/(T-T_s)$.
(a), (b) and (c) correspond to the three cases stated in Figure 3

first category includes (1) inhomogeneity in the static magnetic field and variations in bulk magnetic susceptibility, (2) a distribution of isotropic chemical shifts, and (3) a residual chemical shift anisotropy. The second category contains (1) the so-called natural linewidth, usually determined by modulation of the dipolar interaction by molecular motion, and (2) residual static dipolar interaction. For the film samples, the latter category is a main line-broadening mechanism. ^{13}C line-narrowing is very obvious by increasing temperature or molecular motion. Therefore, the ^{13}C line-narrowing may be in accordance with the model of free volume relaxation. But for the piece sample, all factors, as mentioned above, contribute the ^{13}C line-broadening, even the nonmotional factors dominate. For instance, the linewidth of the carbon 1 at 296K is 429Hz, but linewidth in the film sample is only 235Hz, the difference of 194Hz mainly results from the contribution of the first category. This gives rise to the unsuitability of WLF equation. Cohen's^[9] and Ni's^[10] results show, respectively, that the relations between the ^1H linewidth of melted cis-poly (1,4-butadiene) and the ^{13}C linewidth of poly (1,2-butadiene) and temperature are consistent with WLF equation. These

facts indicate that the polymer relaxation especially due to low frequency molecular motion depends on its free volume.

CONCLUSION

1. The method of latex bidirectional interpenetration is presented for improving the compatibility of polymer blends.

2. The compatibility of PVAc/PBA/PVAc LBIPNs is considerably better than that of the corresponding LIPN and depends to a large extent on the distribution of PVAc both in the core and in the shell.

3. The rotational correlation times of the side-groups of the PBA in 0.5/1/0.5 PVAc/PBA/PVAc LBIPN are longer than those in 1/1 PVAc/PBA LIPN.

4. For the variation in ^{13}C linewidths as temperatures, WLF equation is available for film samples and unsuitable for the piece sample of the LIPN.

Keywords :

Compatibility, Dynamics, Dynamic Mechanical Spectroscopy; ^{13}C Spin-Lattice Relaxation Time and Linewidth; Latex Bidirectional IPN and Latex IPN; Poly(vinyl acetate), Poly(butyl acrylate).

REFERENCES

- [1] Sperling, L. H. and Friedman, D. W., *J. Polym. Sci.*, A2, **1969**, 7, 425.
- [2] Frisch, H. L.; Klempner, D. and Frisch, H. C., *J. Polym. Sci.*, C, **1969**, 775.
- [3] Sperling, L. H., "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, **1981**.
- [4] Kim, S. C.; Klempner, D.; Frisch, K. C.; Frisch, H. L. and Ghiradella, H., *Polym. Eng. Sci.*, **1975**, 5, 339.
- [5] Sperling, L. H., AD 765511.
- [6] Yin, Y. L., Master Thesis, Naval Academy of Engineering, Wuhan China, **1987**.
- [7] Komoroski, R. A. Ed. "High Resolution NMR Spectroscopy of Synthetic Polymer in Bulk", VCH Publishers, **1986**.
- [8] Yan, X., Ph. D. Thesis, Wuhan Institute of Physics, The Chinese Academy of Sciences, **1990**.
- [9] Cohen-Addad, J. P. and Faure, J. P., *J. Chem. Phys.*, **1984**, 61, 1571.
- [10] Ni, S. Y.; Yu, F. S.; Shen, L. F. and Qian, B. G., *Chinese J. Magn. Reson.*, **1986**, 3, 369.