The $T_{1\rho}^{13}$C spin-lattice relaxation time of interpenetrating networks by solid state NMR

Ae Ran Lim$^a$,*, G.T. Schueneman$^b$, B.M. Novak$^c$

$^a$Department of Physics, Jeonju University, Jeonju 560-759, Chonbuk, South Korea
$^b$Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA
$^c$Department of Chemistry, North Carolina State University, Raleigh, NC 27695, USA

Received 23 October 1998; accepted 16 November 1998 by A. Pinczuk

Abstract

Poly (2-hydroxyethyl methacrylate) (PHEMA) and poly(2-hydroxyethyl methacrylate) interpenetrated with 5% SiO$_2$ (PHEMA-IPN) were studied by $^{13}$C CP/MAS NMR. From these results, the structure of two polymers were verified by $^{13}$C NMR. Spin-lattice relaxation times for the polymer carbons in the rotating frame, $T_{1\rho}$, have been measured as a function of temperature. The $T_{1\rho}$ spin-lattice relaxation times of the $\alpha$-quaternary and carbonyl in the PHEMA and PHEMA-IPN undergo slow motions, i.e., motions on the slow side of the $T_{1\rho}$ minimum, while those of the 1-, 2-, $\beta$-methylene, and 3-methyl undergo fast motions, i.e., motions on the fast side of the $T_{1\rho}$ minimum. From these $T_{1\rho}$ spin-lattice relaxation times, we discuss the mobility, the correlation time, and activation energy for the PHEMA and PHEMA-IPN, respectively. The activation energies for the PHEMA-IPN were found to be generally higher than those of PHEMA. The higher activation energy for the side-chain 2-methylene in the PHEMA-IPN is attributed to bonding between the SiO$_2$ and the hydroxyl group of the PHEMA.

© 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Polymers; A. Nanostructures; B. Nano fabrications; B. Chemical synthesis; E. Nuclear resonance

1. Introduction

The sol–gel process [1], with its associated mild conditions, has been used in the synthesis of intimate organic–inorganic composite materials [2]. Of the several synthetic approaches investigated, we have been most interested in simultaneous routes that allow for the formation of mutually-interpenetrating, organic–inorganic network materials [3]. This approach can be illustrated by the synchronous hydrolysis-condensation of tetraalkoxy orthosilicates possessing polymerizable alkoxides and the free radical polymerization of these released olefins (Scheme I).

The degree of phase separation in these composites materials can vary, but domain sizes are typically on the nanometer scale, and in some cases, the are reduced to a level such that true “molecular composites” are formed. As a result of this intimate mixing, these hybrids are often highly transparent, a property which renders them amenable to applications outside the boundaries of traditional composites.

The structure and morphology of these materials has been studied using solid-state NMR (both $^{29}$Si and $^{13}$C), X-ray scattering, Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Analysis (DMA) [4]. The scattering and thermal studies all indicate a high degree of mixing between the two
phases. The DSC spectra of a series of poly (2-hydroxyethyl methacrylate) SiO$_2$ interpenetrating networks (PHEMA-IPN) show the $T_g$ of PHEMA which normally appears at ca. 110°C [5], essentially disappears with loading of SiO$_2$ as low as 10% by weight (~6% by volume) which indicates restricted motion of the main chain. Parallel results are obtained using DMA which shows that incorporating these small amounts of SiO$_2$ within the polymer suppresses the $T_g$ and virtually eliminates the tan δ peak. These pronounced effects indicate that both a high degree of mixing and strong interfacial interactions must be present in these materials. Unfortunately, direct evidence of residual covalent bonds between the SiO$_2$ and the alcohol polymer side chains of PHEMA has not been directly obtained. Using NMR, this information is obscured by broadening and overlap with nearby resonances.

In an effort to address the question of interaction between the 2-hydroxyethyl moiety on PHEMA and the SiO$_2$ phase, we have studied the dynamics of PHEMA within these interpenetrating networks using variable-temperature solid-state $^{13}$C CP/MAS NMR. The results of these studies are reported here.

In this article, we verified the structure of PHEMA and PHEMA-IPN by $^{13}$C CP/MAS NMR. Also, the $^{13}$C spin-lattice relaxation times in the rotating frame, $T_{1p}$, were measured as a function of temperature. From these results, the mobility, correlation time, and the activation energy for each carbon in the respective PHEMA and PHEMA-IPN were measured.

2. Experimental

2.1. Sample preparation

PHEMA/SiO$_2$ IPN materials were prepared following procedures reported previously [3].

2.2. $^{13}$C solid state NMR spectroscopy

The solid state NMR experiments were taken by the previously reported method [6].

3. Results and discussion

The solid state structures and dynamics of PHEMA with and without the interpenetration by SiO$_2$ (5 wt.%) (IPN) were examined using solid state NMR. Fig. 1 shows the solid state $^{13}$C CP/MAS NMR spectrum for PHEMA. The spectrum consisted of six signals at chemical shifts of δ = 179.30, 67.85, 60.92, 56.00, 45.84, and 17.17 ppm at room temperature, and are assigned to 1-, 2-, β-methylene, 3-methyl, α-quatarnary, and carbonyl, respectively. Peak assignments are shown in Fig. 1. Spinning sidebands are marked with asterisks. In the case of the PHEMA-IPN, the $^{13}$C CP/MAS NMR spectrum is similar to the PHEMA. The chemical shifts for both PHEMA and the PHEMA-IPN were measured at various temperatures, and were found to be nearly independent of temperature.

The $^{13}$C spin-lattice relaxation time in the rotating frame, $T_{1p}$, for the PHEMA and PHEMA-IPN were made at various temperatures. Single-exponential
decays are observed for each temperature. The rate of decay of the spin-locked carbon magnetization is characterized [7,8] by the $T_1$ as:

$$M(t) = M_0 \exp(-t/T_1)$$

where $M(t)$ is the resonance at time $t$, and $M_0$ is the resonance intensity at time $t = 0$. The $^{13}$C spin-lattice relaxation times in the rotating frame, $T_{1r}$, is determined by the least-squares fit using the experimental data.

Figs. 2(a) and (b) show $T_{1r}$ for each carbon in both the PHEMA and PHEMA-IPN as a function of temperature. The relaxation times of $\alpha$-quaternary and carbonyl carbons undergo motions on the slow side of the $T_{1r}$ minimum (i.e., under slow motion conditions $\omega \tau_c \gg \omega_1 \tau_c \gg 1$) [9,10]. On the slow side of the $T_{1r}$ minimum a decrease in $T_{1r}$ implies a smaller value of $\tau_c$ and therefore, an increased mobility at higher temperatures. The relaxation times of $1\alpha$, $2\beta$, $\beta$-methylene, and $3\beta$-methyl undergo motions on the fast side of the $T_{1r}$ minimum. These carbons were determined to undergo fast motions.
on the high-frequency side of the $T_\text{1r}_\text{min}$, under fast motion conditions $\omega_1 \tau_c \ll \omega_2 \tau_c \ll 1$. On the fast side of the $T_\text{1r}_\text{min}$, an increase in $T_\text{1r}$ moves to smaller values of $\tau_c$. Therefore, the increase in $T_\text{1r}$ with temperature represents an increase in mobility at higher temperatures for these carbons [11]. In case of $\alpha$-quaternary and carbonyl carbons, the $^{13}\text{C}$ spin-lattice relaxation time in the rotating frame decreases with increasing temperature as shown in Fig. 3. However, $^{13}\text{C} T_\text{1r}$ relaxation times gradually increase as a function of temperature in case of the 1-, 2-, $\beta$-methylene, and 3-methyl carbons. The $T_\text{1r}$ corresponding to six peaks in the PHEMA-IPN have long relaxation times relative to the PHEMA. The $\alpha$-quaternary and carbonyl carbons have relaxation times longer than the 1-, 2-, $\beta$-methylene, and 3-methyl carbons which is consistent with the fact that the dipolar relaxation is more efficient when the carbon has bounded protons [11,12]. The relaxation times of 1-, $\beta$-methylene and 3-methyl carbons similarly increase with increasing temperature for both the PHEMA and PHEMA-IPN. The greatest difference between the PHEMA and PHEMA-IPN samples appear in the alcohol side chains: the relaxation times for the two 2-methylene carbons differ substantially, with the PHEMA-IPN showing the larger value.

The $T_\text{1r}$ values can be related to corresponding values of the rotational correlation time, $\tau_c$ [13].

As such, $\tau_c$ is a direct measure of the rate of motion. For the spin-lattice relaxation time in the rotating frame, the experimental value of $T_\text{1r}$ can be expressed in terms of an isotropic correlation time $\tau_c$ as very rough model for the molecular motions by the following function [14-16];

$$T_\text{1r}^{-1} = (N/20)(\gamma_C \gamma_H h r^{-3})^2 [4J(\omega_1) + J(\omega_1 - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C) + 6J(\omega_H)]$$

(2)
where
\[ J(v_1^H) = \gamma_C \left[ \frac{1 + \omega_1^2 \tau_C^2}{1 + \omega_C^2 \tau_C^2} \right] \]
\[ J(v_1^H - v_1^C) = \tau_C \left[ 1 + (\omega_1^H - \omega_1^C)^2 \tau_C^2 \right] \]
\[ J(v_1^C) = \tau_C \left[ 1 + \omega_C^2 \tau_C^2 \right] \]
\[ J(v_1^H + v_1^C) = \tau_C \left[ 1 + (\omega_1^H + \omega_1^C)^2 \tau_C^2 \right] \]
\[ J(v_1^H) = \tau_C \left[ 1 + \omega_1^2 \tau_C^2 \right] \].

Here, \( \gamma_C \) and \( \gamma_H \) are the gyromagnetic ratios for the \(^{13}\)C and \(^1\)H nuclei, respectively, \( N \) is the number of directly bound protons, \( r \) is the C–H internuclear distance, \( h = h/2\pi \) where \( h \) is Planck’s constant, \( \omega_C \) and \( \omega_H \) are the Larmor frequencies of \(^{13}\)C and \(^1\)H, respectively, and \( \omega_1 ( = 50 \times 2\pi \times 10^3 \text{ rad/s}) \) is the spin-lock field. Therefore, the motion and values of \( \tau_c \) calculated from Eq. (2) are listed in Table 1. The \( \tau_c \) of the \( \alpha \)-quarternary and carbonyl carbons have longer correlation times than other carbons, and the 3-methyl side-chain carbon have shorter correlation times.

Further insight into the correlation times can be gained by examining the activation energies associated with the various carbons. The theoretical temperature dependence of the rate of rotational motions is a simple Arrhenius expression \[ 17,18 \]
\[ \tau_C = \tau_0 \exp\left( \frac{E_a}{RT} \right) \] (3)
where \( E_a \) is activation energy for the molecular motions and \( R \) is the molar gas constant. Thus, a plot of the natural logarithm of the correlation time as a function of the inverse temperature is linear with a slope that is proportional to the activation energy for motion. Fig. 3 shows representative plots of the correlation time as a function of the inverse temperature for 2-methylene carbons in the PHEMA and PHEMA-IPN. The activation energies for all the carbons derived from the slope of the straight line passed through the \( \tau_c \) data are listed in Table 2. From a comparison of these activation energies, the trends become clear. The activation energies for all carbons of the PHEMA-IPN are longer than those measured for the PHEMA. Hence, the molecular motions of PHEMA are restricted by interpenetration of the SiO\(_2\) phase. These measurements are in complete agreement with both the DSC and TMA data which shows a dramatic attenuation of the glass transition temperatures upon interpenetration by SiO\(_2\). Surprisingly, restricted motion of the PHEMA macromolecules occurs at very low loadings of SiO\(_2\); 5 wt.% in this case. This attests to both the high degree of mixing between

![](image)

**Table 1**
The location motion causing relaxation with respect to the \( T_1^a \) minimum and \( \tau_c \) calculated from the value of \( T_1^a \) at 20°C.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>PHEMA side of minimum</th>
<th>( \tau_c ) (s)</th>
<th>PHEMA-IPN side of minimum</th>
<th>( \tau_c ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methyl</td>
<td>fast</td>
<td>( 1.19 \times 10^{-9} )</td>
<td>fast</td>
<td>( 1.23 \times 10^{-9} )</td>
</tr>
<tr>
<td>( \alpha )-quarternary</td>
<td>slow</td>
<td>( 3.77 \times 10^{-6} )</td>
<td>slow</td>
<td>( 3.65 \times 10^{-6} )</td>
</tr>
<tr>
<td>( \beta )-methylene</td>
<td>fast</td>
<td>( 1.48 \times 10^{-8} )</td>
<td>fast</td>
<td>( 1.52 \times 10^{-8} )</td>
</tr>
<tr>
<td>2-methylene</td>
<td>fast</td>
<td>( 5.41 \times 10^{-9} )</td>
<td>fast</td>
<td>( 4.96 \times 10^{-9} )</td>
</tr>
<tr>
<td>1-methylene</td>
<td>fast</td>
<td>( 5.49 \times 10^{-9} )</td>
<td>fast</td>
<td>( 5.91 \times 10^{-9} )</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>slow</td>
<td>( 3.07 \times 10^{-5} )</td>
<td>slow</td>
<td>( 3.38 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
the inorganic and organic phases as well as the strong interfacial interactions that must be present.

The question of residual covalent bonding between the side chain hydroxy group of the PHEMA and the SiO₂ remains open. Unfortunately, no discernable spectroscopic information from the solid-state NMR studies could be uncovered. It is clear, however, that strong interactions, be it covalent C–O–Si linkages or hydrogen bonding, do exist. This is best evidenced by comparing the activation energies of the 2-methylene carbons immediately adjacent to the hydroxyl group in the two samples. The activation energy for the PHEMA-IPN is nearly 4.7 times larger than in PHEMA alone, which indicates substantially restricted motion occurs.

4. Conclusions

The activation energy is a plausibly useful indication of rigidity, and the activation energies for each carbons were obtained from the correlation times as a function of the temperature. Molecular motions in PHEMA interpenetrated with 5% SiO₂ have higher activation energies than in PHEMA alone. Higher activation energies indicates a higher rigidity for the polymer chains in the PHEMA-IPN sample. It is worth noting that the activation energy of the 2-methylene carbon in PHEMA-IPN is distinctly greater than those in PHEMA. This higher activation energy associated with the hydroxy 2-methylene carbon is ascribed to strong interfacial interactions between this group and the SiO₂ phase.

Acknowledgements

One of the authors (A.R. L.) was supported by the KOSEF through the RCDAMP at Pusan National University (1997-2000), and in part by a Jeonju University Faculty Research Grant. B.M. Novak acknowledges the Materials Research Science and Engineering Center at University of Massachusetts, the Office of Naval Research, and the FAA for financial support.

References