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DETERMINATION OF GLASS TRANSITION TEMPERATURE OF POLY(ETHYLENE GLYCOL) BY SPIN PROBE TECHNIQUE

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Abstract—The rotational relaxation data for free nitroxyl radicals in poly(ethylene glycol) samples of mol. wt 3000–22,000 gave for the glass-transition temperature (T_g), a value of −60°, independent of molecular weight. The rotational activation energy was ~2 kJ/mole below T_g and ~10 kJ/mole above T_g. This indicated that the mechanism of motion below T_g differs from the above T_g. Evidently the rotating units of polymer are much smaller below T_g than above it. The rotational relaxation time (τ) was found to be dependent on the molar volume of PEG (V) and to follow the empirical equations $\tau = A \exp(-kV_g)$ and $\tau = B \exp(-kV_1)$, where V_g and V_1 are the molar volumes (cm^3/mol) when $T < T_g$ and T_g and $T > T_g$, respectively, and $k \sim 1$. Therefore the defects in which radicals are located are perhaps the dominant factor determining the dynamic state of probe radicals in polymers at low temperatures.

INTRODUCTION

Several studies on the motions on nitroxyl radically in polymers have been reported [1–6]. However, only few papers concerning the phase transitions in polymers revealed by nitroxyl radicals have been published [7–10]. Earlier we found [11] that spin probe radicals are located in the amorphous phase in poly(ethylene glycol) (PEG). Because the glass transition temperature (T_g) corresponds to the onset of liquid-like translational motions of long segments of molecules in the amorphous phase and the rotations of nitroxyl radicals are sensitive to the changes of geometry in their surroundings, the rotational relaxations of probe radicals in PEG at temperatures near T_g were measured. From earlier studies, it is well known that experiments which are sensitive to the onset of molecular motion in polymer chains (e.g. internal friction, dielectric loss and NMR measurements) may be used to detect the glass transition [12].

RESULTS AND DISCUSSION

The electron spin resonance spectra of a spin probe radical 3-methoxy carbonyl-2,2,5,5-tetramethylpyrroline-1-oxyl (1) in six PEG samples of moderate mol. wt ($\bar{M}_n$ = 3000–22,000. $\bar{M}_w/\bar{M}_n$ = 1·3–1·1) [10] were measured in the range 110K–270 K. The spectra were polycrystalline powder spectra. The rotational correlation times (τ) can be calculated from polycrystalline spectra in the region of slow rotations (10^{-6} sec $> \tau > 10^{-9}$ sec) by means of numerical solutions of diffusion coupled Bloch equations [13] which give the relationship between τ and the shift of the position of the high-field peak with respect to that for infinite viscosity (Δ): Δ = constant × τ exp $(-3/2)$. Another method is based on the stochastic Liouville expression taking into account various rotational models [14]. In this work τ was calculated by the method of McCalley *et al.* [13] from the shift of the position of the high field peak [10]. In Fig. 1 $-\ln\tau$ is given as a function of $1/T$ (K). The scatter in the results is considerable and the plain molecular weight effect is absent. It is well known that T_g is dependent on molecular weight (M_w) [15]. However, the effect of PEG-hydroxyl end groups is opposite to that of $\bar{M}_n$ and therefore it compensates at least partly the $\bar{M}_n$ effect. Therefore in later calculations of this work the mean values of $\ln\tau$ at certain temperature ($<\ln\tau>$) were used. Figure 1 shows that at low temperatures τ is only slightly dependent on T. When the temperature is raised, there is a transition region at $T \sim 213$ K (−60°C). At higher temperatures, τ decreases with increasing temperature. It is evident that the transition temperature −60° represents the T_g of PEG because it appears in the same temperature

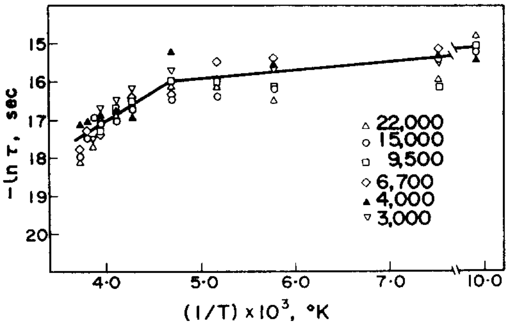

Fig. 1. $1/T$ against relaxation time ($-\ln\tau$) plot of free nitroxyl radicals in poly(ethylene glycols). The $\bar{M}_n$ values of samples are shown.

region as the dynamic mechanical, dielectric and NMR transitions ($-60°$) [16] and T_g values measured by stiffness measurements ($-50°$) [17].

By assuming that the rotation of radicals is a rate process, the activation energies of the process were calculated by means of the Arrhenius equation $\tau = \tau_0 \exp (E_a/RT)$. The values of $E_a \sim 10$ kJ/mole ($T > T_g$) and $E_a \sim 2$ kJ/mole ($T < T_g$) were obtained. These values are far smaller than the apparent activation energies of the viscoelastic processes in the vicinity of T_g (40–320 kJ/mole) [12].

Differing values of E_a below and above T_g mean that the mechanism of molecular motion below T_g differs from that above T_g. The fact that the stiffness of the polymer matrix below T_g is far greater than above it whilst the E_a values are in the reverse order suggests that the motional unit in the former case must be much more smaller than in the latter.

It is notable that $-\ln \tau$ as a function of $(1/T)$ in the region of T_g behaves in the same manner as the relative volumes of polymers in the Simha–Boyer model [19]. According to this model, the real molar volumes of PEG below and above T_g (V_g and V_l respectively) can be calculated from Eqns. (1) and (2):

$$V_g(T) = \epsilon_g T + V_g(0) \tag{1}$$

$$V_l(T) = \epsilon_l T + V_C(0) \tag{2}$$

where ϵ_g ($= 109 \times 10^{-4}$ cm^3/mole K) and ϵ_l($= 282 \times 10^{-4}$ cm^3/mole K) are the molar heat capacities, T is the temperature (K) and $V_C(0)$ and $V_g(0)$ are the zero point volumes. $V_C(0)$ is obtained from an approximate equation $V_C(0) \sim 1{\cdot}3 \times V_w$, where V_w is the van der Waals volume of PEG (24·16 cm^3/mole). $V_g(0)$ can be calculated from known parameters by $V_g(0) = V_g(298) - \epsilon_g \times 298$ where $V_g(298) \sim 1{\cdot}55 \times V_w$. In Fig. 2— $< \ln \tau >$ is given as a function of calculated molar volumes at the temperatures where $\ln \tau$ was measured. A linear relationship between $V_{g,l}$ and $\ln \tau$ is observed*. From the data of Fig. 2 by the method of least squares, empirical equations $\tau = A \exp(-kV_g)$ and $\tau = B \exp(-kV_l)$ are obtained. These equations describe the dependence of τ on molar volume below and above T_g, respectively. Here k is the slope of (V_l, $\ln \tau$) plot. Its numerical value was ~ 1 both below and above T_g.

In the liquid state, the rotational activation energies are of the same order of magnitude as those governing the segmental motions of polymers and it is believed that these segmental motions of polymers determine the rotations of radicals. The results of this work indicate that the rotation of radicals at low temperatures is a volume controlled process. It is probable that radicals are located in defects (holes) in the amorphous phase and that the properties of these defects (e.g. their size distribution and the relaxations in polymer molecules surrounding them) determine the degree of thermal motion of radicals.

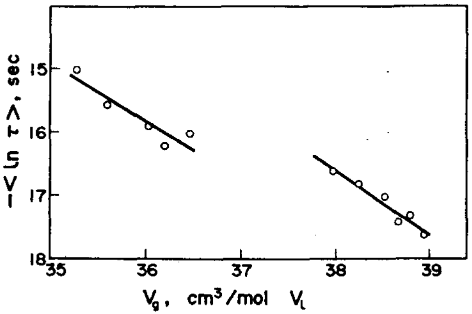

Fig. 2. The dependence of relaxation time ($-\ln \tau$) on the calculated molar volume (V) of poly(ethylene glycol) below T_g (V_g) and above T_g (V_l).

EXPERIMENTAL

The polymer samples were of commercial origin (Fluka and Merck). $\bar{M}_n$ values were measured by a vapour pressure osmometry and their molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were estimated by gel filtration [10]. Spin probe radicals 3-methoxy carbonyl-2,2,5,5-tetramethylpyrroline-1-oxyl (100 ppm) and PEG samples of appropriate molecular weight were dissolved in chloroform, the solvent was distilled away and the samples were dried thoroughly in vacuum. The samples were degassed under vacuum (1×10^{-3} torr) and sealed into ESR-tubes. The ESR spectra were measured by a Varian E-4 X-band spectrometer equipped with a Varian E-257 variable temperature accessory as described earlier [10].

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* This can mean that E_a is an apparent quantity which indicates that the change of τ as a function of temperature is greater above T_g than below it.

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Résumé—L'étude de la relaxation rotationnelle des radicaux libres nitroxyle dans des échantillons de poly(éthylène glycol) de poids moléculaire 3000–22 000, a donné comme température de transition vitreuse T_g) une valeur de $-60°$, qui est indépendante de la masse moléculaire. L'énergie d'activation rotationnelle est de ~ 2 kJ/mole en-dessous de T_g et $\sim$ 10 kJ/mole au-dessus de T_g. Ceci indique que le mécanisme de mouvement au-dessous de T_g est différent de celui au-dessus de T_g. Le nombre d'unités de polymère participant à la rotation est évidemment beaucoup plus faible en-dessous de T_g qu'au-dessus. Le temps de relaxation rotationnel (τ) est indépendant du volume molaire de PEG (V) et suit les équations empiriques suivantes $\tau = A \exp(-kV_g)$ et $\tau = B \exp(-kV_1)$ où V_g et V_1 désignent les volumes molaires (cm^3/mole) respectivement quand $T < T_g$ et $T > T_g$, et $k \sim 1$. Par consequent, les défauts où sont logés les radicaux, constituent peut-être le facteur principal déterminant l'état dynamique des radicaux étudiés dans les polymères à basse température.

Sommario—Per la temperatura di transizione vetrosa (T_g), i dati di rilassazione rotatoria per radicali liberi nitrossilici in campioni di poli(etilene glicolo) di peso molecolare pari a 3000–22.000 hanno fornito un valore di $-60°$, indipendentemente dal peso molecolare. Sotto T_g, l'energia di attivazione rotatoria era di ~ 2 kJ/mole e sopra T_g, di $\sim$ 10 kJ/mole. Ciò indica che il meccanismo del movimento al disotto di T_g differisce da quello al disopra di T_g. Evidentemente i gruppi rotanti del polimero sono molto più piccoli al disotto che al disopra di T_g. Si è trovato che il tempo di rilassazione rotatoria (τ) dipende dal volume molare di PEG (V) e segue le equazioni empiriche $\tau = \mathrm{A}\ \exp^{(-kV_g)}$ e $\tau = B \exp^{(-kV_1)}$, in cui V_g e V_1 sono i volumi molari (cm^3/mole) con $T < T_g$ e T_g e $T > T_g$ rispettivamente, e $k \sim 1$. Di conseguenza i difetti in cui i radicali sono localizzati sono forse il fattore dominante che determina lo stato dinamico dei radicali di prova nei polimeri a basse temperature.

Zusammenfassung—Messungen der Rotationsrelaxation freier Nitroxylradikale in Proben von Polyäthylenglykol mit Molekulargewichten von 3000 bis 22.000 ergaben für die Glastemperatur (T_g) einen Wert von $-60°$, unabhängig vom Molekulargewicht des Polymeren. Die Aktivierungsenergie für die Rotation betrug ~ 2 kJ Mol^{-1}unterhalb T_g und ~ 10 kJ Mol^{-1} oberhalb von T_g. Daraus muss man schliessen, daß der Bewegungsmechanismus unterhalb T_g ein anderer ist als oberhalb. Offenbar sind die rotierende Einheiten des Polymeren unterhalb T_g wesentlich kleiner als oberhalb von T_g.

Die Rotationsrelaxationszeit (τ) ist abhälngig von molaren Volumen von PEG (V) und folgt den empirischen Beziehungen $\tau = A \exp(-kV_g)$ und $\tau = B \exp(-kV_1)$, in denen V_g und V_1 die molaren Volumina (cm^3 Mol^{-1}) sind wenn $T < T_g$ bzw. $T > T_g$ und $k \sim 1$. Deshalb sind wahrscheinlich Fehlstellen, in denen die Radikale lokalisiert sind, der dominierende Faktor, der bei tiefen Temperaturen das dynamische Verhalten von Radikalen in Polymeren bestimmt.