Table I
Free Energy on Microphase Separation of a Diblock Copolymer with $\upsilon_A^c = \upsilon_B^c = 0.5$, $n_A^c = 1000$

χ_{AB}	f_i	$\Delta G/RT$	χ_{AB}	f_i	$\Delta G/RT$
0.05	0	−16.06	0.007	0.2	+0.011
0.05	0.1	−14.48	0.007	0.3	−0.006
0.05	0.2	−12.89	0.007	0.5	−0.024
0.01	0	−1.06	0.007	0.6	−0.027
0.01	0.1	−0.98	0.007	0.7	−0.024
0.01	0.2	−0.89	0.007	0.9	−0.012
0.008	0	−0.31	0.001	0	+2.32
0.008	0.1	−0.30	0.001	0.1	+2.06
0.008	0.2	−0.29	0.001	0.5	+1.10
0.007	0	+0.068	0.001	0.9	+0.21
0.007	0.1	+0.036			

negative of the entropy lost when one molecule undergoes complete microphase separation. This term was derived with the idea that volume fraction υ_A^c of the copolymer suddenly becomes restricted to volume fraction υ_A^c of its original volume and volume fraction υ_B^c suddenly becomes restricted to υ_B^c of its former volume. If volume fraction f_i becomes mixed interphase, then the υ_A^c fraction of the block copolymer becomes suddenly restricted to $\upsilon_A^c(1 - f_i) + f_i = \upsilon_A^c + f_i\upsilon_B^c$ of the sample volume while the υ_B^c fraction of the block copolymers becomes restricted to $\upsilon_B^c + f_i\upsilon_A^c$ of the sample volume. The second term on the rhs of eq 1 therefore becomes

$$-\ln \{\upsilon_A^c + f_i\upsilon_B^c\}^{\upsilon_A^c}\{\upsilon_B^c + f_i\upsilon_A^c\}^{\upsilon_B^c}$$

The last two terms on the rhs of eq 1 will not disappear immediately as the interface becomes less sharp, but the exact form of these terms for diffuse interphases becomes difficult to consider. Although it is probably incorrect in detail to multiply these terms by $(1 - f_i)$, this seems like a reasonable way to let them disappear.

In the presence of a diffuse interface of volume fraction f_i, then, eq 1 reads

$$\Delta G/RT \approx \{-{}^3\!/_4 n_A^c\upsilon_B^c\chi_{AB} + 2(m - 1) - \ln (m - 1)\}\{1 - f_i\} - \ln \{\upsilon_A^c + f_i\upsilon_B^c\}^{\upsilon_A^c}\{\upsilon_B^c + f_i\upsilon_A^c\}^{\upsilon_B^c} \quad (2)$$

Some simple calculations using eq 1 and 2 indicate that free energy considerations of this sort predict sharp boundaries between microphases except when χ_{AB} is close to the value at which complete mixing of the blocks occurs. Calculated values of $\Delta G/RT$ for a diblock copolymer with $\upsilon_A^c = \upsilon_B^c = 0.5$, $n_A^c = 1000$ (a total molecular weight in the vicinity of 200 000), and various values of χ_{AB} and f_i are shown in Table I. For values of χ_{AB} of 0.008 and above, the values of $\Delta G/RT$ are negative for both sharp and diffuse interfaces, but the most negative value is for the sharp interface, thus indicating that free energy considerations favor the sharp interface in these cases. For $\chi_{AB} = 0.007$, $\Delta G/RT$ is positive for the narrow interface, indicating an unfavorable free energy change for microphase separation, and there is a minimum in the negative values of $\Delta G/RT$ at $f_i \approx 0.6$, that is, when 60% by volume of the sample is interphase. That is, the sharp interface hypothesis predicts no microphase separation at all in such a sample, but present considerations indicate a partial phase separation. For $\chi_{AB} = 0.001$, Table I shows positive values of $\Delta G/RT$ for both sharp and diffuse interfaces, so that no phase separation at all is predicted for such a sample.

These calculations may be crude, but they are in accord with experimental observations such as the following. Although T_g's as determined by differential scanning calorimetry (DSC) of microphases generally mimic those of the corresponding homopolymers, the DSC traces of block copolymers that are on the verge of microphase separation show a very broad temperature transition zone which may indicate a diffuse interphase.[14,15]

I have tried to show that both experimental data and theoretical considerations indicate that interfaces between microphases are usually sharp, except when conditions are such that the block copolymer is just on the verge of microphase separation.

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Effect of Stereosequence on Carbon-13 Spin-Lattice Relaxation Times for Poly(vinyl chloride)

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Differences in the spin-lattice relaxation times (T_1) for nuclei in syndiotactic and isotactic configurational sequences have been reported in ^{1}H and ^{13}C NMR studies on poly(methyl methacrylate)[1-4] and in a ^{13}C NMR study on polypropylene.[5] However, Inoue et al.[6] found no dependence of ^{13}C T_1 values on stereosequence for poly(vinyl chloride) in dimethyl-d_6 sulfoxide at 50 °C. We report in this work the measurement of the ^{13}C spin-lattice relaxation times of poly(vinyl chloride) in 1,2,4-trichlorobenzene/p-dioxane-d_8 at 107 °C. The T_1 values of both the methylene and methine carbons are longer for the isotactic sequences than for the syndiotactic sequences.

Experimental Section

The poly(vinyl chloride), Geon 103EP, was obtained from B. F. Goodrich Co. The polymer was observed as a 10% wt/v solution in a 70/20 mixture of 1,2,4-trichlorobenzene and p-dioxane-d_8 at 107 °C. An 18-mm capillary cell was used in the

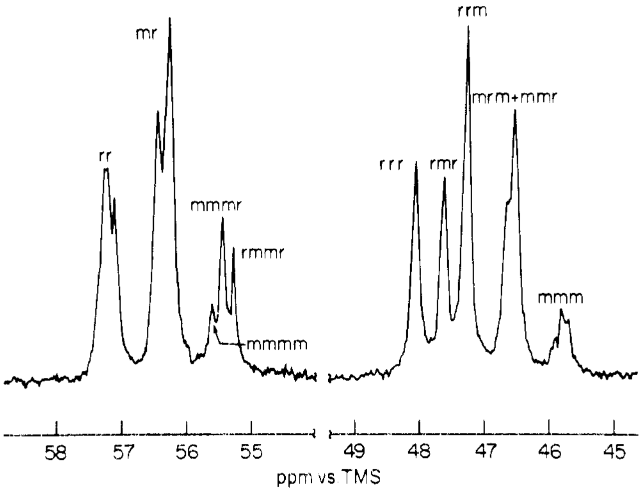

Figure 1. The 25.16-MHz ^{13}C spectrum of poly(vinyl chloride) observed at 107 °C using a 10% wt/v solution in 1,2,4-trichlorobenzene/*p*-dioxane-d_8.

NMR measurement. Spin–lattice relaxation measurements were made on a modified Varian XL-100 spectrometer using the standard inversion–recovery (π–τ–$\pi/2$–T) pulse sequence. An accumulation of 5000 transients was completed for each of the nine τ values used in the measurements. The $\pi/2$ and π pulse widths were 28 μs and 56 μs, respectively. The value of T was greater than $5T_1$ for either carbon. Protons were noise decoupled throughout the measurement. A spectral window of 3012 Hz was used and the resultant FID was stored in 8K computer locations. T_1 values were determined by hand plotting the data. Good linear plots of $\ln (I_\infty - I_\tau/I_\infty) = \ln 2 - \tau/T_1$ were obtained. Essentially identical T_1 values were obtained from the relaxation data by use of a linear regression analysis. We have found for most polymers studied in our laboratory that a reproducibility of ±5% for T_1 results is possible.

Results and Discussion

The 25.16-MHz ^{13}C NMR spectrum of poly(vinyl chloride) is shown in Figure 1. The assignments of the stereosequences are those of Carman.[7] The exact chemical shift data and spin–lattice relaxation times for PVC are given in Table I. The methylene in an isotactic tetrad sequence (*mmm*) has a T_1 which is 24% longer than the T_1 for a methylene in a syndiotactic sequence (*rrr*). If one compares the methine T_1 value for the *mmmm* pentad to that for the methine in the *rr* triad, the difference is 13%. Although these differences are not as large as those found in PMMA, the trend toward longer T_1 values as one moves from completely syndiotactic sequences to completely isotactic sequences is evident from the data. Randall[5] has found for polypropylene a maximum T_1 difference due to stereosequence of 18% for methyl carbons, 44% for methylene carbons, and 51% for methine carbons. Heatley and Begum[1] and Bovey et al.[2] find a 63% difference in the T_1 values of the α-methyl carbon in the *rr* and *mr* sequences of PMMA. The dependence of the T_1 values of PVC on stereosequence is the same as that of polypropylene and PMMA, in the sense that the T_1 values increase in the order of syndiotactic, heterotactic, and isotactic sequences.

Evidently, since the NT_1 values of the methine and methylene carbons are not equal in PVC, even for a given stereosequence, segmental motion is anisotropic. However, if we assume conditions of extreme narrowing and isotropic motion,[8] our data indicate a correlation time on the order of 1.6×10^{-10} s at 107 °C. This value is similar to that for polypropylene under comparable conditions.

Table I
T_1 Values and Chemical Shift[a] Assignments for the Stereoisomers of Poly(vinyl chloride) at 107 °C

stereoisomer	δ ^{13}C	T_1, s
-CH-		
rr	57.21	0.30
rr	57.10	0.30
mr	56.39	0.32
mr	56.24	0.31
mmmm	55.56	0.34
mm *mmmr*	55.41	0.33
rmmr	55.27	0.30
-CH$_2$-		
rrr	48.04	0.17
rmr	47.60	0.18
rrm	47.26	0.18
mmr + *mrm*	46.53	0.18
mmm	45.77	0.21

[a] ppm downfield from Me$_4$Si.

From these results we conclude that the mobility of a backbone bond in PVC depends on its stereosequential environment. This phenomenon is probably a general one, and more careful measurements may reveal a similar dependence of T_1 on stereosequence in other vinyl polymers. Also, the tendency for certain stereosequences to associate in PVC may contribute to the effect.[9]

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$$\frac{1}{NT_1} = \frac{1}{10}\,\frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r^6{}_{C\text{-}H}}\,\chi(\tau_c) \qquad \text{(1a)}$$

where

$$\chi(\tau_c) = \frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c{}^2} + \frac{3\tau_c}{1 + \omega_c{}^2\tau_c{}^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c{}^2} \qquad \text{(1b)}$$

Under conditions of extreme narrowing the dipolar spin-lattice relaxation time is not frequency dependent. The product of $\omega_c\tau_c \ll 1$ and the denominator in eq 1b becomes unity. This reduces eq 1a to the following:

$$\frac{1}{NT_1} = \frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r^6{}_{C\text{-}H}}\,\tau_c$$

which reduces to the numerical expression

$$\tau_c = \frac{4.92 \times 10^{-11}}{NT_1}$$

A complete description of the relaxation equations and terminology is given in J. R. Lyerla, Jr., and G. C. Levy, "Topics in Carbon-13 NMR Spectroscopy", Vol. I, G. C. Levy, Ed., Wiley-Interscience, New York, N.Y., 1974, p 79.
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