Dynamic Carbon-13 NMR Measurements on Poly(vinylidene fluoride) and Poly(methyl methacrylate) and Their Mixed Solutions

F. A. Bovey,*[1] F. C. Schilling,[1] T. K. Kwei,[1] and H. L. Frisch[2]

Bell Laboratories, Murray Hill, New Jersey 07974, and State University of New York at Albany, Albany, New York 12222. *Received November 23, 1976*

ABSTRACT: It is demonstrated that the ^{13}C T_1 values for poly(vinylidene fluoride) and poly(methyl methacrylate) are the same in a mixed solution in *N,N*-dimethylformamide as for solutions containing each polymer alone. It is concluded that the compatibility of these polymers, at least in solution, does not arise from complex formation between them. It is further shown that in poly(vinylidene fluoride) a full nuclear Overhauser enhancement (NOE) is observed for the CH_2 carbons and a zero enhancement for the CF_2 carbons. An explanation for this behavior is offered. Poly(vinylidene fluoride) appears from T_1 and NOE measurements to be a highly flexible polymer, segmental motion being about tenfold faster than in poly(methyl methacrylate). The ^{13}C resonances of the head-to-head and tail-to-tail sequences in poly(vinylidene fluoride) are observed and assigned.

It is well known[3–5] that most polymers are not compatible in the solid state and show only limited mutual miscibility even in solution because the very small gain in entropy is overbalanced by the heat of mixing, which is almost invariably positive. Among the few systems which do exhibit compatibility,[6] both in solution and solid, those involving poly(alkyl methacrylates) and poly(vinylidene fluoride) have aroused particular interest,[7–11] in part because it is intuitively so surprising that compatibility should occur here and also because the poly(vinylidene fluoride) is crystallizable. In an effort to determine if some special interaction such as complex formation occurs between poly(methyl methacrylate) and poly(vinylidene fluoride) in solution we have measured the ^{13}C spin-lattice relaxation (T_1) of each of these polymers alone in *N,N*-dimethylformamide (DMF) and in a mixture of the two in this solvent. Complex formation should impede the segmental motion of the chains and affect T_1. No difference was observed for either polymer alone or in the mixture. Nevertheless, the results are of some interest, particularly for poly(vinylidene fluoride), for which only ^{19}F spectra have been reported heretofore.

Experimental Section

Materials. The poly(vinylidene fluoride), Kynar 821, was obtained from the Pennwalt Corp., Philadelphia, Pa. It had $\overline{M}_w$ of 404 000 and $\overline{M}_n$ of 216 000. It was observed from the ^{19}F spectrum, obtained on a Bruker WH-90 spectrometer, to have a 5.2% content of head-to-head tail-to-tail units.[12] Resonances corresponding to these inverted units are also evident in the ^{13}C spectra (vide infra). Poly(methyl methacrylate), Acrylite H-12, was obtained from American Cyanamid Co., Stamford, Conn.; it had $\overline{M}_w$ of 91 500 and $\overline{M}_n$ of 36 600. It was a typical "atactic" commercial material, i.e., actually predominantly syndiotactic with a $\overline{P}_m$ of ca. 0.20, as determined from the carbonyl spectrum (Figure 1). (These polymers are the same as those described in ref 7.) DMF was reagent grade and was used without further purification.

Methods. The poly(vinylidene fluoride) was observed as a 20% solution and the poly(methyl methacrylate) as a 30% solution in DMF. Equal volumes of these solutions were taken for the mixed solution, giving approximately a 1:1 mole ratio on the basis of monomer units. All observations were made at 41 °C.

T_1 measurements were made by the inversion-recovery method using a Bruker WH-90 instrument. The $\pi/2$ pulse width was 14.5 μs and the π pulse width 29 μs. Protons were noise-decoupled throughout all observations.

For poly(vinylidene fluoride) CH_2 carbon measurements, the spectral window was 1600 Hz and the pulse repetition interval was 1.5 s. The FID was stored in 4K computer locations and 3000 scans were taken for each of 10 points on the T_1 plot. For $^{13}CF_2$ carbon measurements the spectral window was 4000 Hz and the pulse repetition interval was 7.5 s. The FID was stored in 8K locations and 1000 scans were taken for each of seven points.

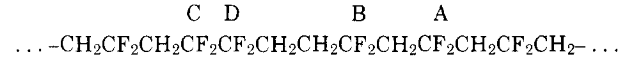
For poly(methyl methacrylate), the observation of the β-CH_2 and α-CH_3 carbons employed a spectral window of 1754 Hz, the FID was stored in 1K locations, the pulse repetition time was 0.30 s, and 16 000 scans were taken for each of 11 points.

In the mixed solutions, measurement of CF_2 and carbonyl carbons employed a spectral window of 5000 Hz and a memory size of 8K, with a repetition time of 6.0 s and 1100 scans for each of seven points. Observation of methoxyl, quaternary, and poly(vinylidene fluoride) CH_2 carbons employed the same conditions except that the repetition time was 2.0 s and 5000 scans were accumulated for each of eight points. For the α-CH_3 and the poly(methyl methacrylate) CH_2 carbons, the spectral window was 1754 Hz, the memory 2K, the repetition time 0.6 s, and 6000 scans were used for each of 13 points.

T_1 values were determined by hand plotting rather than by the use of the Nicolet T_1 program, since machine programs are not in general capable of dealing with partially overlapping resonances. The central resonances of the $^{13}CF_2$ triplet ($J_{^{13}C-^{19}F}$ = 245 Hz) and of the $^{13}CH_2$ pentuplet ($J_{^{13}C-C-^{19}F}$ = ca. 23 Hz) were employed, the latter being only partially resolved (Figure 1). The $^{13}CH_2$ resonance showed a full Overhauser enhancement of 3.0 ± 0.1, whereas the $^{13}CF_2$ resonance showed no enhancement. This observation will be discussed in the next section.

The $^{13}CH_2$ spectrum of poly(vinylidene fluoride), shown in Figure 2, obtained in order to observe the resonances of the head-to-head sequences, was obtained at 90 °C using a 30% (w/v) solution in ethylene carbonate and a Varian XL-100 spectrometer; 20 000 scans were accumulated with a pulse interval of 3 s and a spectral window of 5000 Hz. The $^{13}CF_2$ resonance showed some evidence of these structural irregularities but could not be satisfactorily interpreted.

The T_1 values of the ^{19}F nuclei were measured for poly(vinylidene fluorine) in DMF at 26 °C; 500 scans were accumulated with a pulse interval of 2 s for each of 14 points. In terms of the structure:[12]



$$\ldots\text{–}CH_2CF_2CH_2\overset{C}{CF_2}\overset{D}{CF_2}CH_2CH_2\overset{B}{CF_2}CH_2\overset{A}{CF_2}CH_2CF_2CH_2\text{–}\ldots$$

the following T_1 values (in s) were observed: A, 0.46; B, 0.39; C, 0.39; D, 0.39. Thus, the "defect" fluorine nuclei relax appreciably more rapidly than the normal head-to-tail portions of the chain. We do not at present see any obvious explanation of this result, which is not discussed further in this paper.

Results and Discussion

T_1 Measurements. The ^{13}C spectrum of the mixed solutions of poly(vinylidene fluoride) and poly(methyl methacrylate) is shown in Figure 1. (An inset spectrum shows the carbonyl region, observed with 5000 scans accumulation at 90 MHz on a Bruker HX-360 instrument at 75 °C using a 10% solution (w/v) in $CDCl_3$; this spectrum was employed to establish the $\overline{P}_m$ of this polymer as 0.20.)

The T_1 results for the single and mixed solutions are presented in Table I. Also shown are the effective correlation times τ_c. For poly(methyl methacrylate) these are calculated from eq 1,[13,14] i.e., not necessarily assuming the extreme narrowing limit (although with τ_c taken as less than the reciprocal of the observing frequency ω_c) but, as usual, assuming only dipole–dipole interaction with N bonded protons:

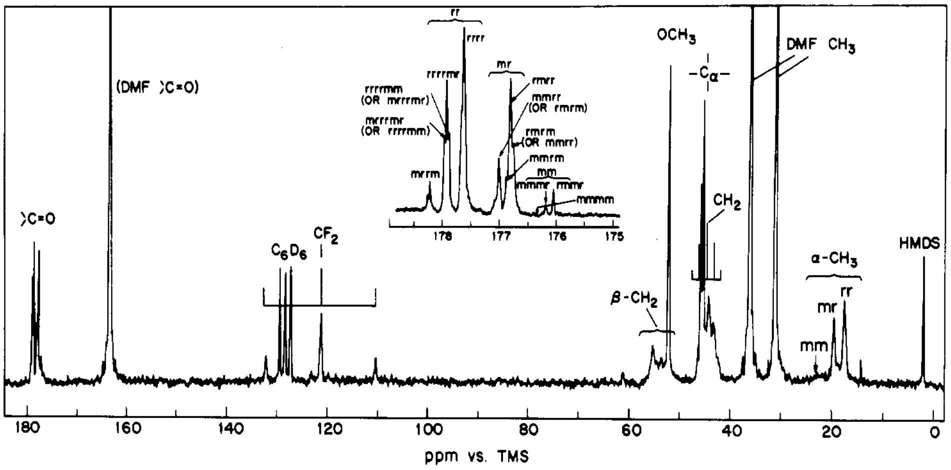


Figure 1. The 22.6 MHz ^{13}C spectrum of a mixed solution of poly(vinylidene fluoride) (10% w/v) and poly(methyl methacrylate) (15% w/v) in DMF observed at 41 °C. The inset spectrum is that of the carbonyl carbons of poly(methyl methacrylate) observed at 90 MHz using a 10% (w/v) $CDCl_3$ solution at 75 °C.

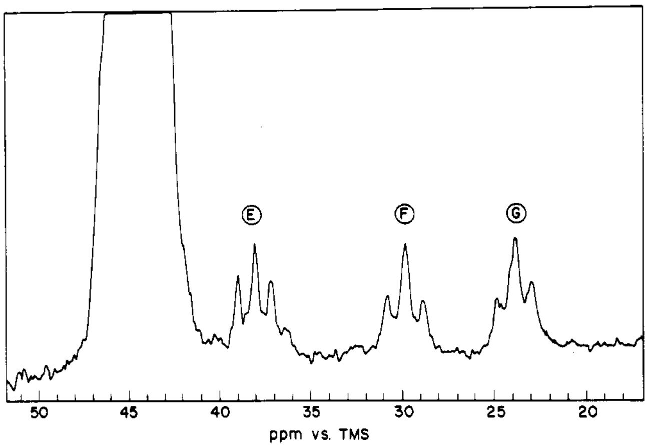


Figure 2. The 25 MHz spectrum of the CH_2 carbons of poly(vinylidene fluoride) observed at 90 °C using a 30% (w/v) solution in ethylene carbonate at 90 °C. The very large resonance centered at ca. 45 ppm is that of the normal head-to-tail sequences. The "defect" resonances E, F, and G are identified in the text.

Table I
T_1 Values and Effective Correlation Times for Poly(methyl methacrylate) and Poly(vinylidene fluoride) in Single and Mixed Solutions in *N,N*-Dimethylformamide at 41 °C

	Single solution		Mixed solution	
^{13}C resonance	T_1, s	τ_c, ns	T_1, s	τ_c, ns
	Poly(methyl methacrylate)			
C=O				
rrrm	1.1_5		1.3_8	
rrrr	1.2_5		1.5_0	
rmrr	1.2_5		1.3_0	
C_α[a]				
mr	0.50		0.47	
rr	0.49		0.48	
C_β (*rrr*)	0.036	0.81	0.037	0.79
α-CH_3[a]				
mr	0.067	0.25	0.056	0.30
rr	0.041	0.43	0.035	0.51
OCH_3	0.48	0.035	0.42	0.039
	Poly(vinylidene fluoride)			
CF_2	1.23	0.077	1.30	0.075
CH_2	0.31	0.079	0.24	0.10_3

[a] The *mm* resonances were too weak for measurement.

$$\frac{1}{NT_1} = \frac{1}{10}\frac{\gamma_H^2\gamma_C^2\hbar^2}{r_{C-H}^6}\chi(\tau_c) \tag{1a}$$

where

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

The other symbols have their usual meanings.

For poly(vinylidene fluoride), the extreme narrowing limit is assumed, because, as will be seen, it exhibits a high degree of segmental mobility. The CH_2 carbons are assumed to be relaxed only by the directly bonded protons (assuming a C–H bond length of 1.10 Å), leading to the well-known[13-15] relationship:

$$\tau_c = \frac{4.92 \times 10^{-11}}{NT_1} \tag{2}$$

For the CF_2 carbons, the greater C–F bond distance of 1.36 Å and smaller ^{19}F magnetogyric ratio result in a substantially longer T_1. It can be readily shown, assuming standard valence angles and either a *trans-trans* or *trans-gauche* conformation for the $-CH_2{}^{13}CF_2CH_2-$ fragment,[16] that in this case the neighboring nonbonded protons cannot be ignored but will contribute about 14% of the relaxation of the CF_2 carbons. The second term in parentheses in eq 3

$$\frac{1}{NT_1} = \gamma_C^2\hbar^2\tau_c(\gamma_F^2 r_{C-F}^{-6} + \gamma_H^2\textstyle\sum r_{C-H}^{-6}) \tag{3}$$

represents this contribution, which, although scarcely outside experimental error, is included in calculating the values of τ_c for CF_2 appearing in Table I. It will be noted that the values of τ_c from CH_2 and CF_2 T_1 measurements are in excellent agreement; indeed, no other result would be reasonable.

For poly(methyl methacrylate) only the *mr* and *rr* triad resonances for the α-methyl and β carbons could be measured, the *mm* peaks being too weak. The β-CH_2 resonance exhibits configurational multiplicity and partial overlap with the OCH_3 peak. The reported T_1 values refer to *r*, principally *rrr*, structures. Of the carbonyl resonances, only *rrrr*, *rrrm*, and *rmrr* could be measured separately; they gave T_1 values which were equal within experimental error. The α-CH_3 groups, however, exhibited a distinct configurational sensitivity, T_1

for *mr* being longer than for *rr*, as already observed by Heatley and Begum.[17] Thus, segmental motion *within the same chain* may be significantly affected by tacticity. Lyerla[18] has demonstrated that the T_1 values for all the measurable carbons of isotactic poly(methyl methacrylate) are markedly longer than those for the syndiotactic polymer. Our values, so far as they can be compared in view of the different solvents employed, are in good agreement with the results of these investigators.

It is recognized[17,19–21] that the single τ_c motional model is not an accurate representation of the behavior of poly(methyl methacrylate) in solution and the same is no doubt true for poly(vinylidene fluoride) as well. However, the effective correlation times reported here are entirely adequate for qualitative and even semiquantitative comparisons of segmental mobility. On this basis, we conclude that poly(vinylidene fluoride) chains are highly flexible, comparable to those of poly(propylene oxide)[17] and polyoxymethylene,[20] and that despite the absence of oxygen "swivel joints", segmental motion is about tenfold more rapid than in poly(methyl methacrylate).

Since their effective correlation times are essentially unaffected when the two polymers are mixed in DMF, it is evident that no appreciable interaction occurs between them which results in complex formation or in collisions which are "sticky" on the scale of the normal segmental reorientation times. Although there thus appear to be no effects due to enthalpy of mutual complexing, the high degree of flexibility of the poly(vinylidene fluoride) tempts one nevertheless to speculate that in some compatible mixtures the effective segment size and coordination number may change so as to produce an additional and favorable contribution to the entropy of mixing beyond that normally expected.

Nuclear Overhauser Enhancement Measurements. It is of some interest that the principal $^{13}CH_2$ resonance of poly(vinylidene fluoride) show a full Overhauser enhancement of 3.0 ± 0.1 whereas the $^{13}CF_2$ resonance show no enhancement (0.06 ± 0.05) within experimental error. (The NOE values of the "defect" resonances in Figure 2 were not measured.) It is commonly observed that all the carbons of a given polymer give equal (but not necessarily full) enhancements, including even those without directly bonded protons.[14,22] The reason for the exceptional behavior of poly(vinylidene fluoride) seems evident, however; the CF_2 carbon nuclei are relaxed by the attached fluorines, which of course are not irradiated. However, the neighboring fluorine dipoles do not detract from the NOE of the CH_2 carbons, because, as we have seen in the discussion of the T_1 results, the dipole–dipole interaction between these nuclei is negligible.

The $^{19}F\ \{^1H\}$ nuclear Overhauser effects in solid poly(vinylidene fluoride) have been described by McBrierty and Douglass.[23] We shall consider the corresponding phenomena in solution in a subsequent paper.

^{13}C Spectrum of Reversed Monomer Units in Poly(vinylidene fluoride). In Figure 2 is shown an expanded 25 MHz $^{13}CH_2$ spectrum of poly(vinylidene fluoride), observed as described in the Experimental Section. The "defect" carbons appear as well-spaced and fairly well-resolved multiplets, all more shielded than the principal resonance. In terms of the chain structure shown,

$$\ldots\text{–}CH_2CF_2CH_2CF_2\overset{E}{CH_2}CF_2CF_2\overset{G}{CH_2}\overset{F}{CH_2}CF_2CH_2CF_2\text{–}\ldots$$

they are assigned to the E, F, and G methylenes in order of increasing shielding. The assignment of E is clear from the pentuplet splitting (23 Hz) arising from four fluorines on neighboring carbons; G and F show the expected triplet splitting (23 Hz) with broadening due to three-bond ^{13}C–^{19}F couplings. The assignments can be rationalized by invoking a deshielding inductive effect by fluorines on neighboring carbons and an opposing fluorine "γ effect" (analogous to the well-known carbon γ effect) for fluorines on next-nearest carbons. The deshielding effect of directly bonded fluorines is evident from Figure 1, in which the $^{13}CF_2$ triplet is about 90 ppm downfield from the methylene resonance in linear polyethylene.[24,25] The deshielding effect of two neighboring CF_2 groups is about 12 ppm, compared to polyethylene, as seen from the principal CH_2 resonance in Figures 1 and 2. If one of the next nearest CH_2 groups is replaced by CF_2, as for E, a *shielding* of ca. 6.5 ppm is observed. For F, the neighbor deshielding and γ effects compensate and the chemical shift is very nearly that of polyethylene. Methylene G is like F except for an additional γ effect and would be expected to be even more shielded than a paraffinic chain, as is observed.

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