affects any chain segment as a whole. In accordance with formula 33, the dependence upon $\lambda^2 - 1/\lambda$ is obtained by assuming that elongation effects determined by $\langle z_{i,j}\rangle^2$ dominate over fluctuation effects determined by $\langle \Delta r_{i,j}^2\rangle$. It must be noted that the relaxation rate dependence upon λ is contrasted to that of the retractive force $f(\lambda)$ since it varies as $\lambda^2 - 1/\lambda$ instead of $\lambda - 1/\lambda^2$.

In accordance with the analysis presented in section II, this nearly general NMR property can be given a framework of description broader than that developed in section III. The transverse nuclear magnetization M_x of the whole gel system is supposed to be a function of $\{\vec{r}_{i,j}\}$ vectors. At a given time t, the derivative of $M_x(t)$ with respect to the stretching ratio λ is expressed as

$$\frac{\partial M_x(t)}{\partial \lambda} = \sum_{i,j} \frac{\partial M_x}{\partial \langle w_{i,j}\rangle}\langle z_{i,j}\rangle - \sum_{i,j} \frac{\partial M_x}{\partial \langle v_{i,j}\rangle}\langle y_{i,j}\rangle / 2\lambda^{3/2} - \sum_{i,j} \frac{\partial M_x}{\partial \langle u_{i,j}\rangle}\langle x_{i,j}\rangle / 2\lambda^{3/2} \quad (34)$$

When a relaxation rate is experimentally found to vary as a $\lambda^2 - 1/\lambda$, its derivative is a function of $2\lambda + 1/\lambda^2$. Compared with equation 34, such a result implies that

$$\frac{1}{2\lambda}\sum_{i,j} \frac{\partial M_x}{\partial \langle w_{i,j}\rangle} = -(\lambda^{1/2})\sum_{i,j} \frac{\partial M_x}{\partial \langle v_{i,j}\rangle} = -(\lambda^{1/2})\sum_{i,j} \frac{\partial M_x}{\partial \langle u_{i,j}\rangle} \quad (35)$$

These equalities correspond to $\partial M_x/\partial\langle w_{i,j}\rangle = \langle w_{i,j}\rangle$-$\partial M_x/\partial\langle v_{i,j}\rangle = -\langle v_{i,j}\rangle$, and $\partial M_x/\partial\langle u_{i,j}\rangle = -\langle u_{i,j}\rangle$, respectively. Accordingly, the magnetization $M_x(t)$ is a function of $2\langle w_{i,j}\rangle^2 - \langle v_{i,j}\rangle^2 - \langle u_{i,j}\rangle^2$ as a whole. Furthermore, the observation of a $\lambda^2 - 1/\lambda$ linear dependence indicates that slow fluctuations of nodes occur in gel systems. Their relaxation rate is probably smaller than 10^{-3} rad·s^{-1} in cross-linked polybutadiene, for example. An affine property applies to the displacements of nodes in gels uniaxially stretched.

V. Conclusion

The present analysis illustrates the relationship existing between the retractive force characterizing a gel system under stretching and the relaxation rate of the transverse magnetization of nuclei attached to polymer chains. More precisely, elongation effects of chain segments connecting nodes and internal fluctuations are involved in both the spin-system response and the retractive force. Also, the nature of the dependence of the magnetic relaxation rate upon the stretching ratio may help in discriminating several gel models from one another. The observed $\lambda^2 - 1/\lambda$ linear dependence of relaxation rates is in accordance with the phantom network model which corresponds to an affine deformation of elastically effective chains and to fluctuations independent of the gel elongation. NMR investigations concern the response of statistical structural units to macroscopic deformations of a gel. This semi-local approach to gel elasticity complements the description derived from mechanical measurements. NMR is very sensitive to the individual fractal character of chain segments resulting from monomer unit–monomer unit interactions and elongation. The $\lambda^2 - 1/\lambda$ dependence of relaxation rates indicates that any chain segment is affected by an affine deformation as a whole, whatever the nature of nodes.

References and Notes

(1) Staverman, A. J. *Adv. Polym. Sci.* **1982**, *44*, 73.
(2) Cohen-Addad, J. P. *J. Phys.* (*Les Vlis, Fr.*) **1982**, *43*, 1509.
(3) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(4) Flory, J. P. *Br. Polym. J.* **1985**, *17*, 96.
(5) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Pergamon Press: New York, 1958.
(6) Callen, H. B. *Thermodynamics*; Wiley: New York, 1966.
(7) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.
(8) Flory, J. P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, N. Y., 1953.
(9) Erman, B.; Monnerie, L. *Macromolecules* **1985**, *18*, 1985.
(10) Deloche, B.; Samulski, E. *Macromolecules* **1981**, *14*, 575.
(11) Gromski, W.; Stadler, R.; Jacobi, M. M. *Macromolecules* **1984**, *17*, 741.
(12) Cohen-Addad, J. P.; Huchot, Ph.; Viallat, A. *Polym. Bull.* **1988**, *19*, 257.
(13) Cohen-Addad, J. P.; Huchot, Ph. *Polymer*, submitted for publication.

Measurement of Homonuclear Coupling Constants Associated with Poly(vinyl fluoride) by ^{19}F Two-Dimensional *J*-Resolved Spectroscopy

Martha D. Bruch*

Polymer Products Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

Received April 1, 1988

ABSTRACT: NMR spectroscopy provides insight into the conformation of synthetic polymers since the magnitudes of the homonuclear scalar coupling constants are sensitive to changes in the average chain conformation. These coupling constants are difficult to extract from conventional spectra since the lines are broad and poorly resolved. Two-dimensional *J*-resolved spectroscopy has been used to measure the ^{19}F scalar coupling constants associated with poly(vinyl fluoride). The magnitude of the scalar coupling constants, and hence the average local conformation, is shown to depend markedly on the local stereochemistry of the coupled fluorines. The local conformation is only slightly affected by the relative stereochemistry of neighboring vinyl fluoride units.

Introduction

NMR spectroscopy is a powerful probe into the microstructure and chain conformation of synthetic polymers because the NMR parameters are sensitive to local structural variations. In particular, homonuclear scalar coupling constants are of interest since the magnitudes of the coupling constants are dependent upon the local chain conformation. However, these coupling constants often are difficult to measure from conventional spectra due to unresolved sequence effects on the NMR parameters that

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* Present address: Department of Pharmacology, University of Texas, Southwestern Medical Center at Dallas, Dallas, TX 75235.

result in the broad lines and spectral overlap typically associated with ^1H or ^{19}F NMR spectra of polymers.

Two-dimensional *J*-resolved (2DJ) spectroscopy is a technique that separates the chemical shift along one axis and the scalar coupling along the other axis of a 2D NMR spectrum. This technique can be used to measure scalar coupling constants even in the case of extreme spectral overlap. 2DJ spectroscopy has been used to measure homonuclear coupling constants in the ^1H NMR spectra of several synthetic polymers including poly(vinyl alcohol),[1,2] poly(propylene oxide),[3] poly(vinyl butyral)[4] and poly(ethylene-*co*-vinyl alcohol).[5] Fluorine-19 2DJ spectroscopy has been used by Cais et al. to measure geminal coupling constants in the ^{19}F spectrum of the adduct of *trans*-1,4-polybutadiene with difluorocarbene.[6] In the current study, ^{19}F 2DJ spectroscopy is used to measure three-, four, and five-bond homonuclear coupling constants in the ^{19}F spectrum of commercial poly(vinyl fluoride) (PVF). This study represents the first application of 2DJ spectroscopy to the measurement of long-range homonuclear coupling constants in the ^{19}F spectrum of a fluoropolymer.

The magnitudes of four-bond coupling constants in the ^{19}F spectrum of isoregic PVF were previously estimated qualitatively from the sizes of the cross-peaks due to four-bond scalar coupling in the ^{19}F COSY spectrum.[7] In this earlier work, the magnitude of these coupling constants was shown to be dependent on the relative stereochemistry of the coupled vinyl fluoride units, and the four-bond coupling constants associated with meso (m) diads were consistently larger than those associated with racemic (r) diads. However, the magnitude of the four-bond coupling constants associated with inverted units in commercial PVF could not be estimated from the COSY spectrum since no cross-peaks due to this interaction were observed. The results presented in the current study confirm that the magnitude of four-bond coupling constants is sequence dependent. In addition, three-, four-, and five-bond coupling constants associated with both normal and inverted units in PVF can be measured from the 2DJ spectrum, and the magnitudes of these *J* values also are shown to be sequence dependent.

Experimental Section

The aregic poly(vinyl fluoride) was supplied by the Aldrich Chemical Co. in powder form and was used without further purification. The ^{19}F 2DJ spectrum was obtained on a 5% solution in *N,N*-dimethylformamide-d_7 (DMF-d_7) at a controlled temperature of 130 °C by using a Bruker AM-300 spectrometer operating at a ^{19}F frequency of 282.4 MHz. The 1D ^{19}F spectrum was obtained on a 8% solution in DMF-d_7 at 130 °C by using a Varian XL-200 spectrometer operating at a ^{19}F frequency of 188.2 MHz. Broad-band proton decoupling was employed in both spectra to remove $^{19}F-^1H$ scalar coupling. For both spectra, a 16-cycle phase-cycling routine was used to minimize spectral artifacts.

The ^{19}F 2D *J*-resolved experiment was performed with a standard spin-echo pulse sequence given by

$$\mathrm{RD}-90°-\frac{t_1}{2}-180°-\frac{t_1}{2}-\mathrm{detect}$$

A total of 128 scans was accumulated by using a relaxation delay of 5 s, which is approximately twice the spin-lattice relaxation time (T_1) for most fluorine signals. Band-pass filters were used in both the observe and decouple channels to enable proton decoupling, and the 90° and 180° observe pulse widths with the filters in line were 18 and 36 μs, respectively. The initial data matrix consisted of 8064 Hz (1024 real data points) in the chemical shift dimension, ω_2, and ±63 Hz (64 real data points) in the scalar coupling dimension, ω_1. In order to improve resolution, the time domain data were multiplied by a sine-bell window function with no phase shift and zero-filled to twice the size in the ω_1 dimension prior to Fourier transformation, and the effective digital resolution after transformation was 7.9 and 1.0 Hz/point in ω_2 and ω_1, respectively. The absolute value (magnitude) spectrum was calculated to convert all peaks in the 2DJ spectrum to positive signals, and the spectrum was "tilted" by 45° so that the ω_1 axis only represents *J* coupling.[9] The tilted spectrum was symmetrized about $J = 0$[10] to eliminate ridges of "t_1 noise" running parallel to the ω_1 axis and other artifacts which arise from pulse imperfections and spectrometer instabilities during the extended acquisition time of the 2DJ experiment (~12 h). Chemical shifts were referenced relative to the shift for mm head-to-tail PVC diads, −178.85 ppm.[7]

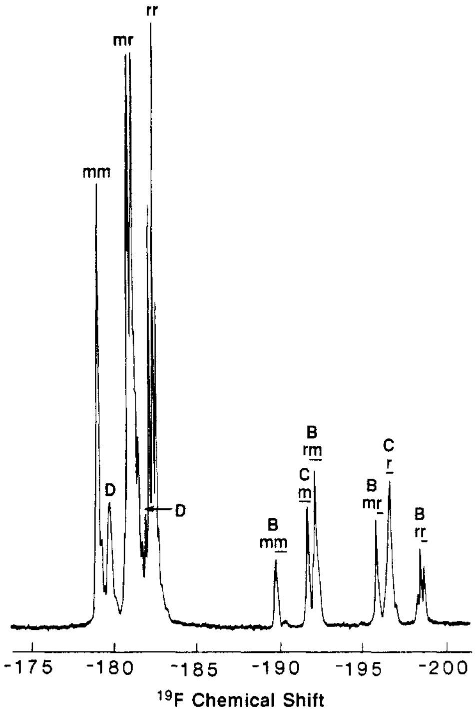
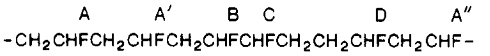


Figure 1. One-dimensional ^{19}F NMR spectrum of poly(vinyl fluoride) obtained with broad-band ^1H decoupling.

Results and Discussion

Commercial poly(vinyl fluoride), an optically clear, highly crystalline plastic, contains a substantial number of head-to-head:tail-to-tail inversions, as first demonstrated by Wilson and Santee.[11] The conventional ^{19}F NMR spectrum, shown in Figure 1, reflects the presence of these inverted units as evidenced by the small peaks in the upfield region of the spectrum. The assignments, idnicated on the spectrum, represent the combined results from several studies.[7,12,13] The main distinct types of fluorines can be described by stereochemical configurations associated with this structure:[7,12,13]



$$-CH_2\overset{A}{C}HFCH_2\overset{A'}{C}HFCH_2\overset{B}{C}HF\overset{C}{C}HFCH_2CH_2\overset{D}{C}HFCH_2\overset{A''}{C}HF-$$

Throughout this discussion, the stereochemical configuration of fluorines in normal (head-to-head) diads is designated as m (meso) or r (racemic), whereas the stereochemical configurations of fluorines B and C in inverted diads are designated as *m* or *r*.[7]

The downfield region of the 2DJ spectrum of PVF is shown in Figure 2. In this spectrum, the horizontal axis, ω_2, reflects only the ^{19}F chemical shift, and the vertical axis reflects only the $^{19}F-^{19}F$ scalar coupling. Hence, a cross section taken through the ω_2 axis contains the subspectrum due only to the fluorine with that chemical shift, and overlapping multiplets can be resolved and observed separately in the 2DJ spectrum. The downfield region con-

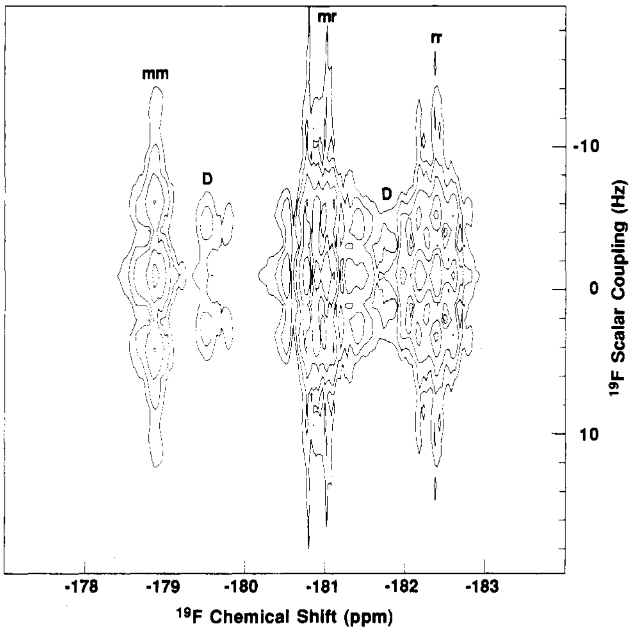


Figure 2. Downfield region of ^{19}F 2D *J*-resolved spectrum of poly(vinyl fluoride) obtained with broad-band ^{1}H decoupling.

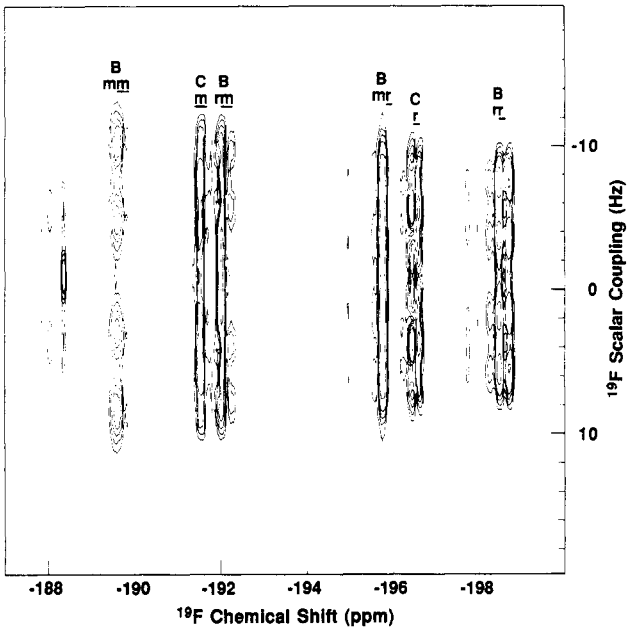


Figure 3. Upfield region of ^{19}F 2D *J*-resolved spectrum of poly(vinyl fluoride) obtained with broad-band ^{1}H decoupling.

tains all the signals due to normal head-to-tail addition (type A fluorines), and the chemical shifts of mm, mr, and rr triads are −178.9, −180.9, and −182.3 ppm, respectively. Type A fluorines have four-bond coupling to fluorines in neighboring vinyl fluoride units on each side, so the resultant multiplet is expected to be either a doublet of doublets (for unequal coupling constants) or a triplet (for equal coupling constants). At the chemical shift corresponding to mm triads, a single triplet is observed (J = 5.0 Hz) in the 2DJ spectrum. For vinyl fluoride units at the center of mm triads, the four-bond coupling is also between fluorines in meso diads. The observation of a single coupling constant implies that the magnitude of the four-bond coupling constant between fluorines in meso diads is constant and is unaffected by longer sequence effects. For rr triads, three triplets are observed at chemical shifts corresponding to rrrr, rrrm, and mrrm pentads and the coupling is always between neighboring fluorines in racemic diads for these sequences; this shows that the magnitude of the constant for racemic diads also is independent of longer sequence effects. Furthermore, these results show that the four-bond coupling constant associated with racemic diads (4 Hz) is significantly less than that associated with meso diads (5 Hz). This confirms earlier qualitative observations from the COSY spectrum[7] and predictions from rotational isomeric-state models[14] that the local chain conformation is different for meso versus racemic diads.

The coupling patterns in the mr region are complex and cannot be readily interpreted since these fluorines are coupled to neighboring fluorines in both meso and racemic diads. The weak multiplets observed in the downfield region also are difficult to interpret. In addition to the dominant signals from type A fluorines, there also are weaker signals expected from fluorines labeled A′ and A″, which correspond to fluorines in normal units directly adjacent to inverted units. These fluorines are quite similar to type A fluorines but have different substituents in the γ and δ positions. The chemical shifts are so similar to that of type A fluorines that these signals cannot be observed readily in the presence of the dominant signals from type A fluorines. Signals from type D fluorines, which differ from type A because a CH_2 group is present instead of a CF_2 group in the β position, also are expected in the downfield region. The small multiplets observed in this region probably are due to type D fluorines. These fluorines have potential four-bond coupling to type A″ fluorines and five-bond coupling to type C fluorines. Two doublets are observed for the type D fluorine signals at −180 ppm (J = 7 Hz). Since the magnitude of the coupling constant generally decreases with distance, the doublets are tentatively assigned to four-bond A″/D coupling. However, specific assignments for these signals are not known, so no definitive conclusions can be drawn.

The upfield region of the 2DJ spectrum, shown in Figure 3, contains multiplets due to B and C fluorines, and the assignments are indicated on Figure 3. The multiplet due to B fluorines in m*m* triads at −190 ppm is a doublet of doublets with coupling constants of 13.0 and 5.2 Hz. Since B fluorines in m*m* triads have vicinal coupling to C m*m* fluorines and four-bond coupling to A′ fluorines in m diads, the larger coupling constant (13.0 Hz) is attributed to vicinal B/C coupling and the smaller coupling constant (5.2 Hz) to four-bond A′/B coupling. An entirely different pattern is observed for C *m* fluorines at −191.5 ppm: a doublet of triplets with coupling constants of 13.1 Hz (doublet) and 3.0 Hz (triplet). The larger splitting must be due to vicinal coupling to B *m* fluorines, and the coupling constant measured from this multiplet is in excellent agreement with the value measured from the multiplet corresponding to B m*m*. The smaller coupling must be due to five-bond coupling to the fluorines on both sides (types A′ and D).

There has been some question in the past as to the assignment of the peak at −191.5 ppm,[12,13] but the observed coupling pattern at this chemical shift confirms that this peak is due to type C, not type B, fluorines. The assignment of this peak to all C *m* fluorines poses some difficulties since this peak is not large enough (relative to B m*m* and B r*m* peaks) to account for all of the C *m* intensity. Previously, the peak at −192 ppm was assigned to B r*m* fluorines, but some fine structure associated with this peak was observed in the COSY spectrum.[7] In agreement with the COSY results, two distinct multiplets are observed near −192 ppm in the 2DJ spectrum, and these multiplets differ in chemical shift by only 0.2 ppm. The more upfield multiplet, at −192.2 ppm, is a doublet of doublets characteristic of type B fluorines, so this multiplet must be due to B r*m* fluorines. The other multiplet in this region, at −192.0 ppm, is too complex to be due to type B fluorines; it must be due to type C fluorines. Therefore, this multiplet at −192.0 ppm is assigned to C r*m* fluorines, and the multiplet at −191.5 ppm is assigned to C m*m* fluorines. This overlap of B and C r*m* fluorines and the splitting of C *m* fluorines into two peaks explain the prior controversy regarding the assignments in this region, and this spectral overlap also explains the absence of definitive cross-peaks connecting B and C r*m* fluorines in the COSY spectrum.[7] In addition, the relative intensities of all the peaks are consistent with these new assignments.

The vicinal (B/C) and four-bond (A′/B) coupling constants measured from the multiplet due to B r*m* fluorines (−192.2 ppm) are 12.7 and 3.5 Hz, respectively. The vicinal coupling constant is only slightly different from that observed for B m*m* sequences, so the average dihedral angle between B and C fluorines is affected only slightly by the relative spectrochemistry of fluorines A′ and B in the neighboring head-to-tail linkage. By contrast, the four-bond coupling constant is much less for m*m* sequences (5.2 Hz) than for r*m* sequences (3.5 Hz). This is consistent with the results obtained for type A fluorines and shows that the average local chain conformation is different for meso versus racemic diads.

The multiplets in the *r* region can be interpreted in a similar manner to those in the *m* region. B m*r* fluorines give rise to a doublet of doublets with vicinal and four-bond coupling constants of 9.2 and 4.8 Hz, respectively. Some fine structure in the chemical shift dimension is observed, and this probably reflects partial resolution of longer sequence effects. Similarly, B r*r* fluorines give rise to three doublet of doublets patterns centered at −198.4 ppm. The chemical shifts differ by 0.2 ppm, but the magnitudes of the vicinal and four-bond coupling constants remain constant at 9.0 and 3.3 Hz, respectively. The fine structure reflects longer sequence sensitivity, but specific assignments are not known. The constant nature of the coupling constants supports the earlier observation that the local conformation is not significantly affected by the relative stereochemistry of neighboring units. As further evidence, the B/C vicinal coupling constants for m*r* and r*r* differ only slightly. By contrast, the chain conformation is quite sensitive to the relative stereochemistry of the fluorines that are coupled. The B/C vicinal coupling constant for *m* inverted diads (~13 Hz) is much larger than that observed for *r* diads (~9 Hz), so the average dihedral angle must be different for meso versus racemic inverted diads. This is consistent with that observed for type A fluorines in normal diads and suggests a difference in the relative populations of the rotational conformers. Similarly, the four-bond coupling constant for A′/B in m*r* sequences (4.8 Hz) is much greater than that observed for r*r* sequences (3.3 Hz), and this is consistent with results obtained on type A fluorines.

Those same results are reflected in the coupling patterns observed for the C *r* fluorines. The B/C vicinal coupling constants measured from C m*r* and r*r* multiplets are in excellent agreement with those measured from the multiplets for B m*r* and r*r* and confirm the assignments made from the COSY spectrum.[7] The five-bond coupling constants to A′ and D fluorines are not equal for the m*r* and r*r* C fluorines, and the magnitude of the coupling constants is sequence dependent.

Now that the magnitudes of the coupling constants are known, the absence of corss-peaks connecting the isoregic region to the defect region in the COSY spectrum can be rationalized. The intensity of cross-peaks corresponding to a specific interaction in a COSY spectrum is dependent upon the number of these interactions, the magnitude of the coupling constant for this interaction, and the magnitude of all other coupling constants associated with the nuclei involved in the interaction. The intensity of a cross-peak is reduced by the multiplication factor given by the product of cos ($\Pi J_i t$) for all other coupling constants, J_i, associated with the observed nucleus (other than the coupling constant for the interaction of interest).[15] For the type A fluorines, all of the coupling constants are due to four-bond coupling and are of a similar magnitude. However, type B fluorines have vicinal coupling constants much larger than the four-bond A′/B coupling constants. Hence, the intensities of the A′/B cross-peaks are significantly diminished relative to the intensities of the B/C cross-peaks. This effect in combination with the increased complexity of the fine structure associated with the cross-peaks, the small number of defect structures present in the polymer chain, and the poor digital resolution associated with the COSY spectrum conspires to make the four-bond A′/B cross-peaks too small to detect. Similarly, the five-bond A′/C and C/D interactions are too small to detect in the COSY spectrum.

Table I
^{19}F Chemical Shifts and Coupling Constants for PVF

assignment	chemical shift,[a] ppm	J_3,[b] Hz	J_4, Hz	J_5, Hz
A mm	−178.85		5.0	
A rr	−182.1, −182.3, −182.5		4.0	
B m*m*	−189.6	13.0	5.2	
B r*m*	−192.2	12.7	3.5	
B m*r*	−195.7	9.2	4.8	
B r*r*	−198.2, −198.4, −198.6	9.0	3.3	
C m*m*	−191.5	13.1		3.0
C r*m*	−192.0	*c*		*c*
C m*r*	−196.4	9.4		3.0, 3.9
C r*r*	−196.5	9.0		~2.5

[a] Chemical shifts referenced to A mm shift of −178.85 ppm. [b] J_3 refers to vicinal B/C coupling, J_4 refers to four-bond A/A or A′/B coupling, J_5 refers to five-bond A′/C or C/D coupling. Uncertainty is ±0.2 Hz. [c] Coupling constants cannot be measured due to complexity of multiplet.

Conclusions

The three-, four-, and five-bond ^{19}F homonuclear coupling constants between neighboring units in PVF were measured from the 2DJ spectrum, and the results are summarized in Table I. The magnitudes of these coupling constants depend strongly on the relative stereochemistry of the coupled fluorines, but little dependence on the stereochemistry of neighboring units is observed. This shows that the average local chain conformation is primarily dependent upon the local stereochemistry. The magnitude of the four-bond coupling constants associated with fluorines adjacent to inverted diads (A′/B) is not affected significantly by the presence of the defect structure, and this supports previous predictions from the rotational isomeric-state model for PVF that the conformations of the bonds in the head-to-tail linkage are not affected significantly by the presence of type C fluorines.[14]

The results obtained in this study support previous observations and provide more detailed information which can be used to rationalize seemingly anomalous results obtained previously. The coupling patterns observed for B and C fluorines in the *m* region allow definitive assignments to be made. These new assignments are consistent with the relative intensities of the peaks in this region and resolve the apparent discrepancies noted earlier. The 2DJ results also explain the absence of expected cross-peaks between the isoregic and defect regions in PVF. The four-bond A′/B coupling constants are significantly less than the vicinal B/C coupling constants, so the B/C cross-peaks are observed at the expense of the A′/B cross-peaks.

Registry No. PVF, 24981-14-4.

References and Notes

(1) Macura, S.; Brown, L. R. *J. Magn. Reson.* **1983,** *53,* 529.
(2) Gippert, G. P.; Brown, L. R. *Polym. Bull. (Berlin)* **1984,** *11,* 585.
(3) Bruch, M. D.; Bovey, F. A.; Cais, R. E.; Noggle, J. H. *Macromolecules* **1985,** *18,* 1253.
(4) Bruch, M. D.; Bonesteel, J. K. *Macromolecules* **1986,** *19,* 1622.
(5) Bruch, M. D. *Macromolecules,* in press.
(6) Cais, R. E.; Mirau, P. A.; Siddiqui, S. *Br. Polym. J.* **1987,** *19,* 189.
(7) Bruch, M. D.; Bovey, F. A.; Cais, R. E. *Macromolecules* **1984,** *17,* 2547.
(8) Aue, W. P.; Karhan, J.; Ernst, R. R. *J. Chem. Phys.* **1976,** *64,* 4226.
(9) Brownstein, S. *J. Magn. Reson.* **1981,** *42,* 150.
(10) Mersh, J. D.; Sanders, J. K. M. *J. Magn. Reson.* **1982,** *50,* 171.
(11) Wilson, C. W., III; Santee, E. R., Jr. *J. Polym. Sci., Part C* **1965,** *8,* 97.
(12) Tonelli, A. E.; Schilling, F. C.; Cais, R. E. *Macromolecules* **1982,** *15,* 849.
(13) Weigert, F. J. *Org. Magn. Reson.* **1971,** *3,* 373.
(14) Tonelli, A. E.; *Macromolecules* **1980,** *13,* 734.
(15) Bax, A.; Byrd, R. A.; Aszalos, A. *J. Am. Chem. Soc.* **1984,** *106,* 7632.

Macroporous Gels. 5. A Differential Scanning Calorimetry Study of the Formation of Macroporous Gels Containing Trimethylolpropane Trimethacrylate

J.-E. Rosenberg and P. Flodin*

Department of Polymer Technology, Chalmers University of Technology,
S-412 96 Gothenburg, Sweden.

Received May 21, 1987;
Revised Manuscript Received May 24, 1988

ABSTRACT: The free radical homopolymerization of trimethylolpropane trimethacrylate (TRIM) and the free radical copolymerization of TRIM and methyl methacrylate (MMA) in solution were studied by DSC. The kinetic order of reaction and the activation energy were determined by both isothermal and dynamic measurements. Calculations of the activation energy from isothermal and dynamic measurements were in good agreement, as were results from homopolymerization and copolymerization experiments (about 20 kcal/g). The reactions were shown to be of nearly first order, which is in fair agreement with the results of previous NMR measurements.

Introduction

The polymerization of trimethylolpropane trimethacrylate (TRIM) in a solvent often results in macroporous gels.[1,2] It is possible to vary the structure of these resins by polymerization in different solvents and by copolymerization with suitable monomers.[2,3]

Differential scanning calorimeter (DSC) is a powerful tool in evaluating the kinetics of a polymerization. Simple methods for calculating the activation energy and the kinetic order of reaction from both dynamic and isothermal measurements have been described in the literature.[6-9]

The purpose of this paper is to study the formation of poly(TRIM) through the evolution of heat during the polymerization. Performing a polymerization in a DSC apparatus makes it possible to follow the whole reaction continuously. The behavior of the TRIM homopolymerization and the TRIM–MMA copolymerization in two different solvents (toluene and ethyl acetate) will be described. This is important for the understanding of polymerizations in which large amount of TRIM monomer are present.

A comparison of the results obtained with a previous investigation of the polymerization of trimethylolpropane trimethacrylate by ^{1}H FT NMR[4] will also be made.

Experimental Section

Polymerization (DSC Studies). In homopolymerization experiments, trimethylolpropane trimethacrylate (TRIM, technical quality containing more than 98% TRIM from Merck AG and Alfa Products) was mixed with a solvent (toluene or ethyl acetate, analytical grade), while in the copolymerization experiments methyl methacrylate (MMA, analytical grade) was also included. The mixture was transferred into a 50-mL hypo-vial containing 0.1% (w/w) azobis(isobutyronitrile) (AIBN, analytical grade). In the following, mixtures will be given in volume percent.

Nitrogen gas was bubbled through the solution for at least 1 min and then the vial was sealed. A sufficient amount (about 20 mg) of the solution was then transferred into a DSC high-pressure steel sample cup (Perkin-Elmer, no. 319-0218) and placed in the DSC cell.

Kinetic Measurements with DSC. The in situ DSC experiments were carried out in two different ways, by dynamic (scanning) and by isothermal measurements. The isothermal measurements were performed at four different temperatures, 343, 348, 353, and 358 K. The four heating rates in the dynamic measurements were 0.62, 1.25, 2.5, and 5.0 K/min. Indium was used for temperature and calorimetric calibration. All experiments were carried out under a constant flow of nitrogen through the DSC cell. An empty high-pressure steel sample cup was used as a reference. The instrument used for the measurements was a Perkin-Elmer DSC-2.

Results and Discussion

Theoretical Considerations. By DSC one measures the rates of heat absorption or evolution (dH/dt) of a sample compared to a reference when the temperature is raised at a constant rate. It is also possible to make the measurements under isothermal conditions. It is possible to calculate the activation energy and the kinetic reaction order of the polymerization reaction by evaluating both the dynamic and the isothermal (DSC) thermograms.[5-9] The first method was partly proposed by Barton[6] and is based on multiple isothermal experiments at different

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* To whom correspondence should be addressed.

0024-9297/89/2222-0155$01.50/0