

## Microstructural Studies of Vinylidene Fluoride–Hexafluoroacetone Copolymer

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**ABSTRACT:** Free radical copolymerization using a peroxide as initiator was carried out to prepare the copolymer of vinylidene fluoride (VDF) and hexafluoroacetone (HFA). The monomer reactivity ratios of  $r_1=4.0$  and  $r_2=0.1$  were obtained by Fineman–Ross method. The microstructure for comonomer sequence of the VDF–HFA copolymer was determined by high resolution  $^{19}\text{F}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR, and infrared spectra. It was found that HFA unit exists mainly in the form of  $-\text{CH}_2-\text{CF}_2-\text{C}(\text{CF}_3)_2-\text{O}-$  in the backbone chain. In the DSC measurement, it was found that the amorphous region in the copolymer decreases with increasing HFA content.

**KEY WORDS** Vinylidene Fluoride–Hexafluoroacetone Copolymer / Monomer Reactivity Ratio /  $^{19}\text{F}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR / Spin Decoupling / Microstructure / Differential Scanning Calorimetry /

In recent years high resolution nuclear magnetic resonance has been successfully applied for the conformational analysis of monomer unit and the determination of the average configurational arrangement of substituent groups along the backbone chain in several fluoropolymers.<sup>1–5</sup> Naylor and Lasoski first mentioned the result of observations on polymeric fluorine chemical shift, using the  $^{19}\text{F}$  NMR spectra, for identification of poly(vinyl fluoride), poly(vinylidene fluoride) (PVDF), and poly(trifluoroethylene). Therefore, many authors has been reported the results on structural analysis of monomer sequence distribution for many kinds of fluorine containing homopolymers and copolymers.<sup>6–9</sup> In particular, detailed analysis allowed to assign occasional Head to Head structure of PVDF<sup>3,5,10,11</sup> in the polymer chain. In these structural studies of the fluoropolymers,  $^{19}\text{F}$  NMR spectroscopy was powerful, since the chemical shifts of  $^{19}\text{F}$  nuclei are considerably greater than those of proton nuclei and many common nondeuterated solvents can be used

for the measurement.

On the other hand, the radical reactivity of HFA<sup>12,13</sup> the representative of fluoroketons, has been investigated to allow the reaction with simple olefins such as ethylene, vinyl acetate and vinyl fluoride,<sup>12</sup> to form mainly polymeric products having the highly branched structure with  $-\text{OH}$  group.<sup>14</sup> Moreover, it has been reported that HFA makes the linear chain structure with tetrafluoroethylene.<sup>12</sup> However, as for the copolymer of VDF and HFA, a few patents described only the formation of copolymers,<sup>15,16</sup> and the microstructure of VDF–HFA copolymer has not yet been studied. In addition, the monomer reactivity ratios and the resulting sequential structures has been scarcely described. Thus, the purpose of this study is to clarify the detailed microstructure and the thermal property of the VDF–HFA copolymer. This kind of fluorocarbon polymer having HFA unit may be useful for industrial objects such as optical materials and other functional polymers.

## EXPERIMENTAL

*Sample Preparation*

VDF and HFA copolymers were prepared in free radical copolymerization in 1,1,2-chlorotrifluoro-1,2,2-fluorotrichloroethane at 25°C using heptafluorobutylic peroxide as initiator. The copolymerizations up to a high conversion of 60% were carried out for the structural analysis, whereas those under 15% conversion were carried out to figure out monomer reactivity ratios. These copolymers were precipitated in distilled water from acetone solution, and volatile material was thoroughly removed under vacuum condition.

*Measurements*

The VDF–HFA copolymer compositions were determined by using elementary analysis of Perkin-Elmer 2400 elemental analyzer.

Structural analysis of the copolymer were performed with a high resolution  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectroscopy on FX90A of JEOL Ltd. And  $^{13}\text{C}$  NMR was measured using JNM-GSX270N of JEOL Ltd. Infrared measurements were done on Hitachi 270-30 Infrared Spectrophotometer.

Thermal property was investigated by use of differential scanning calorimetry (DSC) of Rigaku Denki Ltd., at a heating rate of  $10^\circ\text{C min}^{-1}$ .

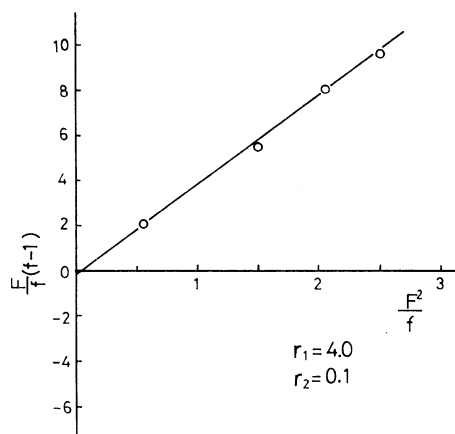
## RESULTS AND DISCUSSION

*Monomer Reactivity*

The results of copolymer composition dependence of polymerization time in VDF–HFA copolymer are summarized in Table I. In three experimental conditions with different monomer composition, HFA mol% consumed to form the copolymer sequence was found about one third of the monomer composition; but the other two third was not consumed by the copolymerization. Thus, the radical reactivity of HFA to make the polymeric product may be poor. These copolymers are soluble in

**Table I.** Polymer composition dependence of reaction time for VDF–HFA copolymers

Monomer composition	Polymer composition in 3 reaction time		
	VDF/HFA		
VDF/HFA	1 h	6 h	24 h
90/10	97.3/3.0	96.6/3.4	96.6/3.4
85/15	95.5/4.5	95.0/5.0	95.0/5.0
70/30	91.0/9.0	90.0/10.0	89.8/10.2

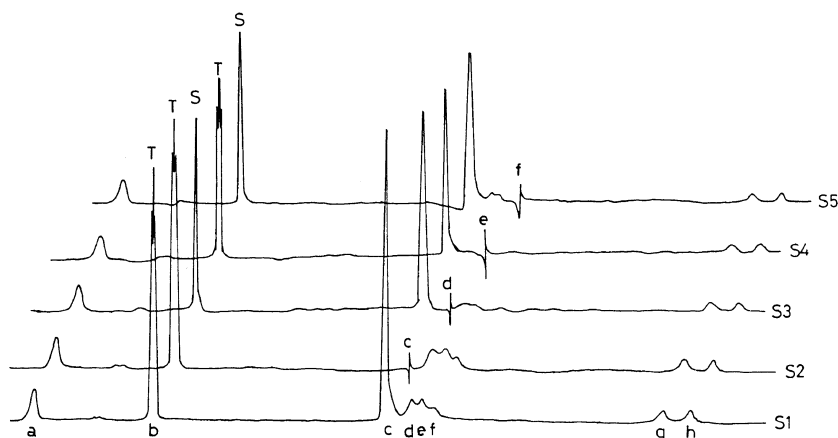


**Figure 1.** Monomer reactivity ratios of  $r_1$  and  $r_2$  in the copolymerization of VDF ( $M_1$ ) and HFA ( $M_2$ ).

many kinds of organic solvents such as acetone, several esters and THF, though VDF homopolymer was soluble in only dipolar aprotic solvents, such as DMA, DMF, and DMSO. The monomer reactivity ratios,  $r_1$  (VDF)=4.0 and  $r_2$  (HFA)=0.1 at 25°C were calculated by the Fineman–Ross method as shown in Figure 1. Both results of Table I and Figure 1 suggest that the radical reactivity of HFA is much less than that of VDF in whole reaction time of copolymerization and both monomers are arranged at random along the polymer chain.

*Copolymer Microstructure*

Figure 2 shows  $^{19}\text{F}$  NMR spectra of VDF–HFA copolymer (HFA=10.2 mol%). This spectra of the copolymer were obtained by  $^{19}\text{F}$  homospin-decoupling technique in

$^{19}\text{F}$ -NMR

**Figure 2.**  $^{19}\text{F}$  NMR spectra for VDF-HFA copolymer (HFA = 10.2 mol%) with homo-spin decoupling technique: S1 shows original  $^{19}\text{F}$  NMR spectrum, and S2-S5 are decoupled with peaks c, d, e, and f, respectively.

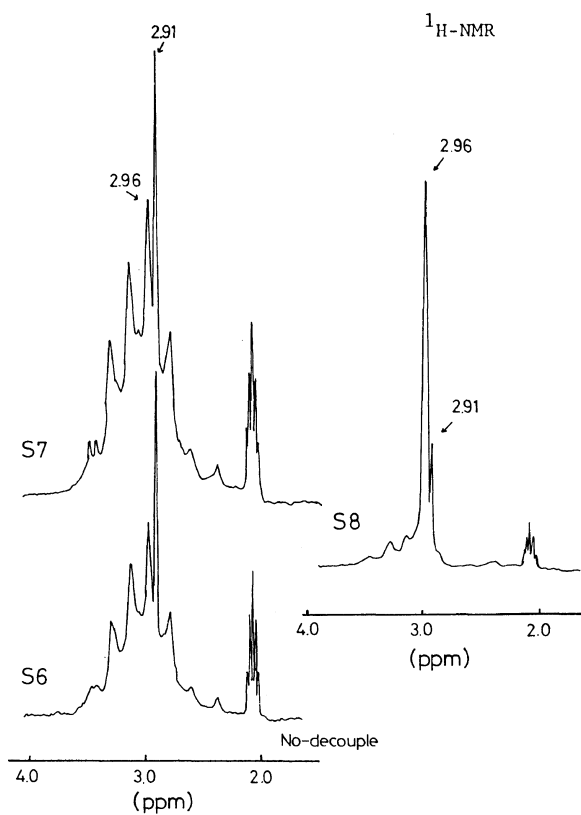
**Table II.**  $^{19}\text{F}$  NMR chemical shifts average values of VDF-HFA copolymer

Peak Sequence by Wilson <sup>5</sup>	Chemical shift from $\text{CFCl}_3$
	ppm
a	62.9
b	72.7
c $-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$	92.0
d	94.0
e $-\text{CH}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$	94.9
f	95.7
g $-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-$	114.3
h $-\text{CH}_2-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CH}_2-$	116.6

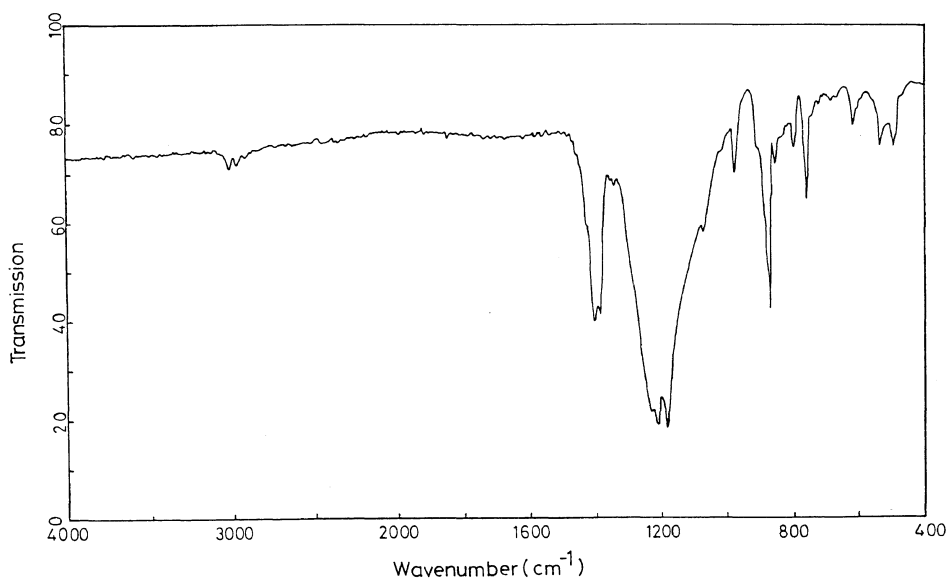
Peaks c, e, g, and h are same as the Wilson's values in PVDF.

5 wt% of acetone- $d_6$ . Original spectrum S1 shows eight observable peaks of which the chemical shift values from standard peak of  $\text{CFCl}_3$  are shown in Table II. In the case of PVDF, the  $^{19}\text{F}$  NMR spectrum has been investigated by Wilson and Santee.<sup>5</sup> They reported the spectrum consisted of the four peaks with the chemical shifts at 91.0, 93.0, 112.5, and 115.0 ppm from  $\text{CFCl}_3$ . These four

peaks are, thus, almost the same values as peaks c, e, g, and h in Figure 2, respectively. In accordance with them, the four peaks have been assigned to the possible sequences containing 5 carbon atoms along the polymer chain, and the presence of head-to-head structure which corresponds to our peaks of e, g, and h has also been demonstrated. Thus, the new observable peaks of a, b, d, and f in Figure 2 are necessary to consider the microstructure of VDF-HFA copolymer. In particular, it is important that the peak b is a triplet. Spectra S2 to S5 in Figure 2 show the  $^{19}\text{F}$  NMR spectra obtained by the homospin-decoupling technique irradiating the four frequencies corresponding to the magnetic fields of peaks c, d, e, and f, respectively. According to the decoupling technique, triplet b changed to singlet b by the irradiation of peaks d and f. These observations involve an additional information for explaining particular arrangement of VDF and HFA in the chain. It indicates that peak b corresponds to  $-\text{CF}_3$  of HFA, and peaks d and f are  $-\text{CF}_2-$  where is the side position of carbon atom of HFA unit. Therefore, the presence of  $-\text{CF}_3$  group



**Figure 3.**  $^1\text{H}$  NMR spectra for VDF-HFA copolymer (HFA=10.2 mol%) in acetone- $d_6$  under 3 conditions: S6 is no spin decoupling, S7 and S8 are decoupled with peaks b and c of  $^{19}\text{F}$  NMR.



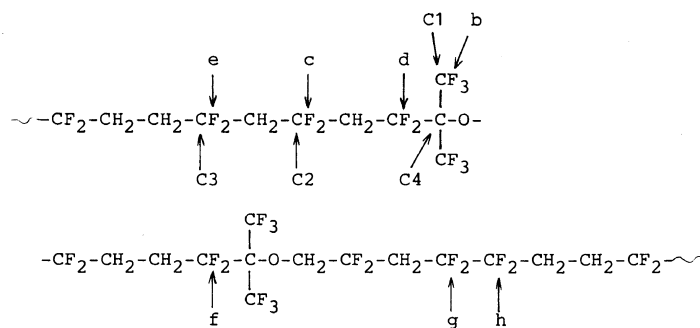
**Figure 4.** Infrared spectrum for VDF-HFA copolymer (HFA=10.2 mol%).

connecting  $-\text{CF}_2-$  group at second neighboring position was suggested.

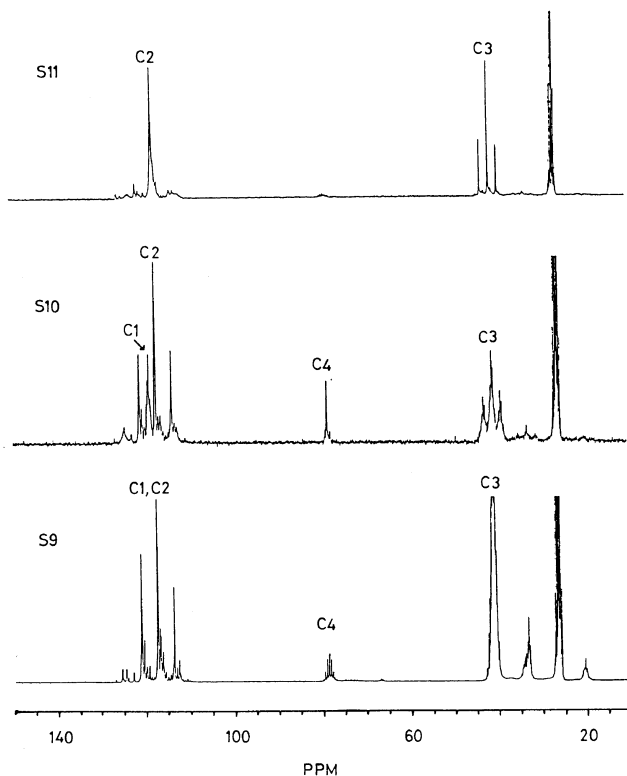
Figure 3 shows  $^1\text{H}$  NMR spectra of the VDF-HFA copolymer (HFA = 10.2 mol%) in acetone- $d_6$  under 3 conditions: S6 is no  $^{19}\text{F}$  spin-decoupling, and S7 and S8 are decoupled peaks b and c of the  $^{19}\text{F}$  NMR spectrum shown

in Figure 2, respectively. The spectra clearly lead to two facts that there are not any coupling between  $-\text{CF}_3$  of HFA and proton of VDF, and the copolymer has a very symmetrical  $-\text{CF}_2-$  configuration flanked on both sides by  $-\text{CH}_2-$  group.

Infrared spectrum of VDF-HFA copolymer



**Figure 5.** VDF-HFA copolymer molecular chain structure proposed by NMR and IR measurements, where a-h and C1-C4 denote the peaks in Figures 2 and 6, respectively.



**Figure 6.**  $^{13}\text{C}$  NMR spectra for VDF-HFA copolymer (HFA = 10.2 mol%): S9 is an usual  $^1\text{H}$  complete decoupling spectrum, and S10 and S11 are measured by  $^{19}\text{F}$  selective spin decoupling with peaks b and c.

(HFA = 10.2 mol%) is shown in Figure 4. Since -OH absorption is not observed in this spectrum, a branched HFA as the substituent of copolymer chain does not exist, although the side chain with -OH was reported in the case of copolymerization of HFA and ethylene.<sup>12</sup> Thus, it was supported that the hydrogen abstraction giving terminal positions on the branches did not occur in the case of copolymerization of VDF and HFA.

The result of these structural studies in Figures 2 to 4 was consequently attributed to the microstructure of an ether bond such as  $-\text{CF}_2-\text{C}(\text{CF}_3)_2-\text{O}-$  in the copolymer chain. The most conceivable structure of the VDF-HFA copolymer is, therefore, proposed as that in Figure 5.

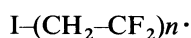
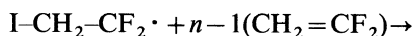
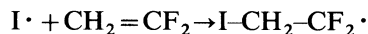
The molecular structure corresponding to peaks b to h of S1 in Figure 2 are illustrated in this monomer linkages. An empirical rule, that  $-\text{CF}_2-$  position shifts to downfield by coupling with other F atom of second neighboring position, was then applied for the distinction between the assignments of peaks d and f.

Another evidence for the proposed molecular chain structure was obtained by a  $^{13}\text{C}$  NMR measurement. Figure 6 shows  $^{13}\text{C}$  NMR spectra of VDF-HFA copolymer (HFA = 10.2 mol%) in acetone- $d_6$  under 3 conditions. S9 was an usual  $^1\text{H}$  complete decoupling spectrum, and S10 and S11 were measured by  $^{19}\text{F}$  selective spin-decoupling technique irradiating peaks b and c in Figure 2, respectively. In these spectra, many peaks corresponding to  $-\text{CF}_2-$  and  $-\text{CF}_3$  were observed at the downfield range of 110 ppm and 130 ppm, and also several peaks for  $-\text{CH}_2-$  were observed at upfield range of almost 40 ppm. These assignments were able to facilitate further discussion by the decoupling with  $^1\text{H}$  and  $^{19}\text{F}$  nuclei. In this figure, C1, C2, C3, and C4 represent the carbon atoms in the molecular structure in Figure 5. Most interesting view is seen in the fact that a multiplet of C4 in the  $^1\text{H}$  complete decoupling  $^{13}\text{C}$  NMR spectrum changes to a triplet by the

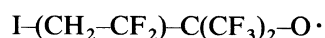
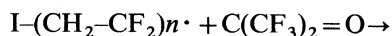
technique decoupled with peak b of  $^{19}\text{F}$  NMR spectrum. This triplet is an evidence demonstrated by the microstructure of  $-\text{CF}_2-\text{C}(\text{CF}_3)_2-$  which is already described in Figure 5. In other words, it seems that the multiplet for quaternary carbon of C4 in  $^1\text{H}$  decoupling method transfers the triplet spin-coupled only with F atom of the neighboring  $-\text{CF}_2-$  unit. Therefore, it was found that the proposed molecular chain structure is undoubtedly reasonable and the structure is essentially different from that of HFA-ethylene copolymer which is not completely linear but contains amount of carbon branching.

However, in this study on the microstructure of VDF-HFA copolymer, three problems remain unsolved. The first problem is an assignment of peak a in S1 of  $^{19}\text{F}$  NMR spectrum. The second problem is that either of  $-\text{CH}_2-$  or  $-\text{CF}_2-$  is assigned to other side of ether bond against the quaternary carbon of HFA. The last problem is the possibility of the presence of  $-\text{CF}_2-\text{CH}_2-\text{C}(\text{CF}_3)_2-\text{O}-$  in the chain. These significant problems should be discussed in future.

Based on these sequential features of the microstructure of VDF-HFA copolymer, the following reaction schemes are considered. This free-radical copolymerization proceeds as follows: normal initiation and propagation steps.



The reaction of HFA monomer with VDF radicals takes place following to a radical attack at the carbon of carbonyl system to give the structure of  $-\text{CF}_2-\text{C}(\text{CF}_3)_2-$ .



This hexafluoroisopropyl radical may continue to react with VDF monomer. That is because the radical end group would be high elec-

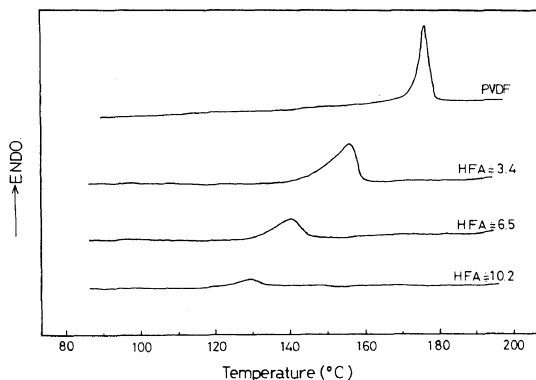


Figure 7. DSC thermograms for the 3 different compositions of VDF-HFA copolymers.

trophilic in effect of the electron attraction of the two  $-\text{CF}_3$  groups. Thus, the oxygen radical can react with VDF but not with the electron poor HFA.

#### Thermal Properties

Figure 7 shows a characteristic thermogram of DSC exhibiting an endotherm of melting behavior. In contradistinction to the melting transition of PVDF, these melting points in three different VDF-HFA copolymers depress with increasing HFA content in the copolymer, and shift to low temperature. These melting transition behaviors are probably associated with the presence of HFA unit expanding the distance of crystal lattice in VDF sequence. This is simultaneously able to consider an

increasing of amorphous region.

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#### REFERENCES

1. R. E. Naylor, Jr. and S. W. Lasoski, Jr., *J. Polym. Sci.*, **44**, 173 (1960).
2. R. C. Ferguson, *J. Am. Chem. Soc.*, **82**, 2416 (1960).
3. C. W. Wilson, III, *J. Polym. Sci., A*, **1**, 1305 (1963).
4. G. V. D. Tiers and F. A. Bovey, *J. Polym. Sci., A*, **1**, 833 (1963).
5. C. W. Wilson, III and E. R. Santee, Jr., *J. Polym. Sci., Part C*, No. 8, 97 (1965).
6. J. G. Pritchard, R. L. Vollmer, W. C. Lawrence, and W. B. Black, *J. Polym. Sci., A-1*, **4**, 707 (1966).
7. K. Fujii, S. Brownstein, and A. M. Eastham, *J. Polym. Sci., A-1*, **6**, 2387 (1968).
8. K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **3**, 27 (1970).
9. T. Yagi and M. Takemoto, *Polym. J.*, **11**, 429 (1979).
10. R. Liepins, J. R. Surlis, N. Morosoff, V. T. Stannett, M. L. Timmons, and J. J. Wortman, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 3039 (1978).
11. A. E. Tonell, *Macromolecules*, **9**, 547 (1976).
12. J. F. Harris, Jr. and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 1553 (1962).
13. W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964).
14. E. G. Haward and P. B. Sargeant, *J. Macromol. Sci. Chem.*, **A1**, 1011 (1967).
15. E. G. Haward, French Patent 1436591.
16. E. G. Haward, British Patent 1020678.