TABLE III
RESULTS OF INTERSEQUENCE CYCLIZATION IN METHYL METHACRYLATE–BUTADIENE COPOLYMERS

Sample	% M[a]	Relative resonance areas,[b] %				f_c (MMA)	
		A	B	A′	B′	Exptl	Theor[c]
H-1	72.5	36.1	63.9	29.3	70.7	0.33	0.28
H-2	61.0	35.5	64.5	26.4	73.6	0.50	0.50
H-3	55.0	34.6	65.4	23.2	76.8	0.66	0.70
H-4	41.5	35.1	64.9	23.4	76.6	0.86	0.88
H-5	30.0	33.3	66.7	24.9	75.1	0.91	0.95

[a] Average of compositions obtained through elemental and nmr analysis. [b] See text for definitions of *A*, *A′*, *B*, *B′*. [c] Based on monomer reactivity ratios of 0.73 and 0.18 for butadiene and methyl methacrylate, respectively.

respectively, these values being determined by the Fineman–Ross[17] and Mayo–Lewis[18] procedures from the compositions of the copolymers and the polymerization mixtures. These values are to be compared with corresponding values of 0.53 ± 0.05 and 0.06 ± 0.03 determined by Walling and Davison[19] for the copolymerization of butadiene with methyl methacrylate at 5°.

Experimentally determined f_c values (eq 3) are in good agreement with theoretical values, indicating that the spontaneous lactonization which occurs during the bromination of butadiene–methyl methacrylate copolymers obeys the statistical treatment of random intersequence cyclization reactions. It seems likely that the brominative cyclization reaction described in this paper will prove useful for characterizing the structures of other copolymers and terpolymers containing diene and acrylate or methacrylate units.

Acknowledgments. The authors are indebted to The Mobil Chemical Co. and the National Science Foundation (GP-5908) for supporting this project. In addition, we are grateful to Mr. E. R. Santee, Jr., for recording the 100-MHz nmr spectra used in this work.

---

(17) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
(18) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
(19) C. Walling and J. A. Davison, *ibid.*, **73**, 5736 (1951).

Kinetics of Propagation of Living Poly-2-vinylpyridine

M. Fisher and M. Szwarc

Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210. *Received August 21, 1969*

ABSTRACT: Kinetics of homopropagation of living poly-2-vinylpyridine has been thoroughly investigated in THF and, less extensively, in other ethereal solvents. In addition we studied the conductance of the homopolymer solutions and of solutions of analogous polymers built from styrene units but terminated by single pyridine units. The results allowed us to determine the rates and the activation energies of the free $\sim\sim(2\text{-VP})^-$ ions and of $\sim\sim(2\text{-VP})^-,\text{Na}^+$ ion pairs, as well as the dissociation constants and heats of dissociation of the living polymers. Comparison of the systems $\sim\sim(2\text{-VP})^-,\text{Na}^+$ and sodium living polystyrene led to interesting conclusions about intra- and intermolecular solvation of ion pairs. In the latter case, solvent may separate an ion pair, thus increasing its dipole moment. The larger dipole moment makes the pairs more reactive and the separation facilitates its dissociation. The intramolecular solvation by partially immobile groups also increases its dipole moment by "stretching" the pair. This enhances its reactivity, but because the cation is bound to the solvating groups of the polymer its dissociation is hindered. The latter effect reduces somewhat the reactivity of the pair although such a retarding factor is less significant than the enhancing one arising from the increase of the dipole.

Kinetics of homopolymerization of 2-vinylpyridine was studied by Lee, *et al.*[1] Their work was limited to sodium salts in THF at 25°, and no attempt was made during that investigation to differentiate between free ions and ion pairs. We repeated now this study using a more versatile technique described elsewhere[2] and determined the propagation rate constants for the free ions and ion pairs over a wide temperature range (−60 to +25°). Moreover, a few kinetic experiments were performed in THP and dioxane in order to evaluate the effect of solvent on the rate of propagation. Also, in some preliminary runs Cs^+ salts were used instead of Na^+.

Experimental Section

Commercial 2-vinylpyridine was distilled at reduced pressure on a spinning band column and its purity ascertained by vpc analysis. The distilled monomer was dried by digesting it with CaH_2, the product distilled on a high-vacuum line into a bulb containing fresh CaH_2, and finally redistilled into ampoules equipped with break-seals in

---

(1) C. L. Lee, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, **59**, 1192 (1963).
(2) T. Shimomura, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 796 (1967).

Table I

Dissociation Constant of $\sim(2VP)^-,Na^+$ and $\sim S\cdot(2VP)^-,Na^+$

Temp, °C	$10^9K_d[\sim(2VP)^-,Na^+]$, M	$10^9K_d[\sim S\cdot(2VP)^-,Na^+]$, M
25	0.87 (0.8)[a]	6.2
20	0.94	6.3
10	1.2	7.1
0	1.4 (1.4)[a]	7.8
−10	1.6	8.9
−20	2.0 (2.2)[a]	10
−30	2.4 (2.8)[a]	11
−40	3.2 (3.7)[a] at −43°	13
−50	3.8	
−60	4.7	
−70	6.5	

[a] The revised dissociation constants determined by Professor Sigwalt (private communication). Solutions of $\sim 2VP^-,Na^+$ and $\sim S\cdot(2VP)^-,Na^+$ in THF show differences in their uv and visible spectra; a small shift in λ_{max}, *viz.*, from 315 to 317 mμ, and a shoulder in the region of 450 mμ pronounced in the homopolymer but absent in $\sim S\cdot(2VP)^-,Na^+$. The spectrum of the homo $\sim 2VP^-,Cs^-$ resembles that of the latter polymer but λ_{max} 318 mμ.

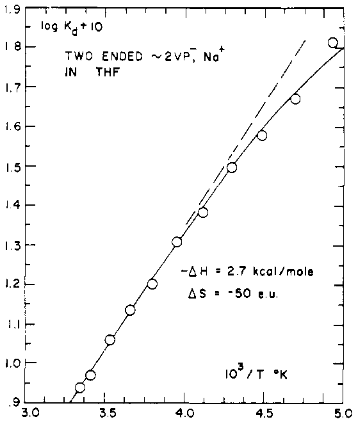

Figure 1. Temperature dependence of the dissociation constant of living sodium poly-2-vinylpyridine endowed with two active ends, solvent THF.

which the monomer was stored. The latter were sealed off from the vacuum line and used as required.

Living sodium poly-2-vinylpyridine (two-ended) was prepared in THF by reacting the monomer with sodium–α-methylstyrene tetramer. The THP and dioxane solutions were obtained by replacing THF with the desired solvent. Traces of THF do not affect the reactivity of those solutions because equally reactive were the samples of living polyvinylpyridine initiated with the dimeric dianoins of 1,1-diphenylethylene which in turn were directly prepared in THP. It was demonstrated that the excess of 2-vinylpyridine was sufficiently large to ensure a complete conversion of $-D^-,Na^+$ into $-2-VP^-,Na^+$. Several attempts to prepared the polymer in THP using α-methylstyrene tetramer as the initiator failed. Apparently in this solvent the $-^-C(CH_3)(Ph)$ carbanions attack the pyridine moieties and consequently the resulting polymer becomes cross-linked. It is interesting to note that this complication is not observed in THF, in spite of the fact the homopropagation is *faster* in THP than in THF (see Results).

The cesium polyvinylpyridine was prepared in THF by treating the monomer with cesium α-methylstyrene dimer.

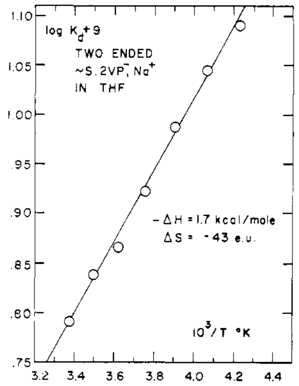

Figure 2. Temperature dependence of the dissociation constant of a living polymer built from styrene units and possessing only one pyridine moiety on each of its ends, solvent THF, counterion Na^+.

The initiator was synthesized by reacting α-methylstyrene in THF with the metal.

Conductance of polystyrenes terminated with one and with two units of sodium 2-vinylpyridine was investigated. The former polymer was prepared at −70° by slowly evaporating 2-vinylpyridine onto a stirred THF solution of living polystyrene possessing two active ends. About 10% excess of the monomer was used and the spectrum of the final solution showed that all $\sim S^-,Na^+$ was converted into $\sim S\cdot(2VP)^-,Na^+$. It seems that the interaction of $\sim S^-,Na^+$ with the ring of the pyridine moiety was prevented by the low temperature and by the negative charge residing on the pyridine units. The technique of our conductance and kinetic studies was described earlier.[2]

Results

Conductance Studies. The dissociation constants, K_d, of $\sim(2\text{-}VP)^-,Na^+$ and of $\sim S\cdots S(2\text{-}VP)^-,Na^+$ in THF are much lower than those of sodium polystyrene.[2] The results (Table I) were obtained from Fuoss plots, using the Λ_0 obtained for living polystyrene.[2] The temperature dependence of K_d is shown in Figures 1 and 2 and the heats of dissociation were found to be −2.7 kcal/mol ($\Delta S = -50$ eu) and −1.7 kcal/mol ($\Delta S = -43$ eu) for $\sim(2\text{-}VP)^-,Na^+$ and $\sim S\cdot(2\text{-}VP)^-,Na^+$, respectively. The reliability of the data is confirmed by the independent studies of Professor Sigwalt,[3,4] who investigated the dissociation of $\sim(2\text{-}VP)^-,Na^-$ possessing one and two active ends. The agreement between his and our studies is most satisfactory (see Table I).

The problem may be raised whether intramolecular formation of triple ions contributes to the dissociation of sodium polyvinylpyridine in THF. Such a phenomenon was observed for cesium polystyrene[5] but not for the sodium salt.[2] It manifests itself by a difference in the dissociation constants of the polymers possessing two and one living ends, respectively,[5] but otherwise being identical. A recent study by Professor Sigwalt's group[4] showed that sodium polyvinylpyridine dissociates to the same extent in THF whether endowed with

---

[3] M. Tardi, D. Rouge, and P. Sigwalt, *Eur. Polym. J.*, **3**, 85 (1967).

[4] P. Sigwalt, private communication.

[5] D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **86**, 5024 (1964); see also D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

TABLE II

HOMOPOLYMERIZATION OF POLY-2-VINYLPYRIDINE$^-$,Na$^+$ IN THF. [2-VINYLPYRIDINE]$_0$ $\sim 10^{-3}$ *M*; *T* = 25°

[L.E.] × 10^5, *M*	k_{obsd}, M^{-1} sec^{-1}	[L.E.] × 10^5, *M*	k_{obsd}, M^{-1} sec^{-1}	[L.E.] × 10^5, *M*	k_{obsd}, M^{-1} sec^{-1}
26	2230	7.1	2470	2.9	2610
17	2440	6.8	2590	2.9	2520
14	2250	6.6	2480	2.8	2460
12.5	2400	5.4	2780	2.4	2810
11.5	2520	5.1	2640	2.4	2970
11.0	2360	5.0	2590	1.9	2920
8.8	2340	4.4	2580	1.7	2860
T = 0°		*T* = −20°		*T* = −60°	
83	736	28	301	79	12.7
23	768	15.5	296	48	13.7
22	732	10.2	304	39	15.0
11.5	801	5.4	315	30	13.5
5.6	817	5.1	321	12.6	13.3
3.7	788	2.7	330	4.4	17.9

TABLE III

HOMOPOLYMERIZATION OF POLY-2-VINYLPYRIDINE$^-$,NA$^+$ IN THF[a]

Temp, °C	$k_\pm$, M^{-1} sec^{-1}	k_-, M^{-1} sec^{-1}
25	2100 ± 150	100,000 ± 30,000
0	720 ± 40	14,000 ± 4,000
−20	280 ± 40	6,000 ± 2,000
−60	12 ± 2.5	500 ± 100

[a] $E_\pm = 7.7 \pm 0.2$ kcal/mol; $A_\pm = 10^9$ M^{-1} sec^{-1}. $E_- = 7.8 \pm 1.0$ kcal/mol; $A_- = 4 \times 10^{10}$ M^{-1} sec^{-1}.

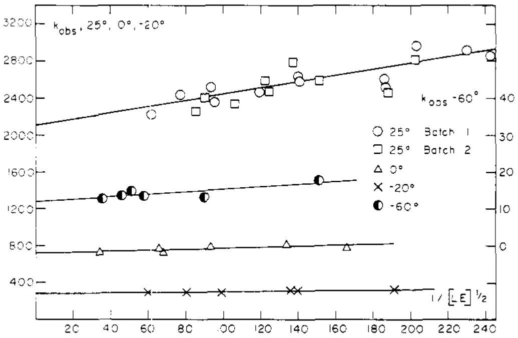

Figure 3. Plots of k_{obsd} *vs.* 1/[LE]$^{1/2}$ for ~~~(2-VP)$^-$,Na$^+$ in THF: ○ and □, two different batches of polymer investigated at 25°; △, the results at 0°; ×, the results at −20°; ◐, the results at −60° (scale of the letter given on the right.)

one or two growing ends, the relevant dissociation constants being determined for a wide temperature range from −43 to +23°. It seems, therefore, that the intramolecular formation of triple ions is negligible in this system, and hence the intermolecular association into such ions should be also negligible. Nevertheless, we observed a much larger curvature in the Fuoss plots obtained from the conductance data pertaining to the polyvinylpyridine system than from those obtained for the polystyrene system. No explanation is offered for this behavior.[6]

Results of the Kinetic Studies. The observed homopropagation constants, k_{obsd}, for sodium poly-2-vinylpyridine in THF at 25° are much larger than those found for sodium polystyrene.[2] The pertinent data are collected in Table II which includes also the results obtained at lower temperatures. The plots of k_{obsd} *vs.* 1/[LE]$^{1/2}$ are shown in Figure 3 and the least square lines give the "best" values for the relevant intercepts and slopes. The former are interpreted as the propagation constants of ion pairs, $k_\pm$, the latter, in conjunction with K_d's, allow us to calculate the propagation constant, k_-, of the free ~~~(2-VP)$^-$ ions. These constants are collected in Table III and the Arrhenius plots are shown in Figures 4 and 5. We find $E_\pm$ = 7.7 ± 0.2 kcal/mol, $A_\pm = 10^9$ M^{-1} sec^{-1}, E_- = 7.8 ± 1 kcal/mol, and $A_- = 4 \times 10^{10}$ M^{-1} sec^{-1}.

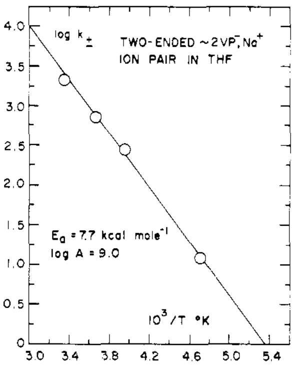

Figure 4. Plot of log $k_\pm$ of ~~~(2-VP)$^-$,Na$^+$ ion pair in THF *vs.* 1/T.

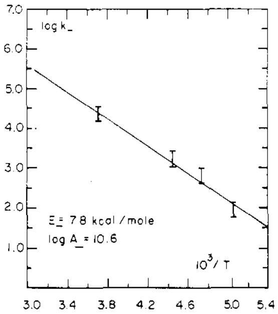

Figure 5. Plot of log k_- of ~~~(2-VP)$^-$ free ion in THF *vs.* 1/T.

At 25° k_{obsd} varies from 2200 to 3000 M^{-1} sec^{-1}. Previous studies carried out in this laboratory[1] led to values ranging from 2900 up to 7000 M^{-1} sec^{-1}. Although the highest constants were considered then as the most significant, we feel now that this conclusion is questionable, and the lower values of k_{obsd} seem to be genuine. It is probable that technical difficulties encountered in the determination of small amounts of vinylpyridine (see Table I of ref 1) led to some erroneous results.

In several experiments the rates of polymerization were determined in the presence and absence of sodium tetraphenylboride and hardly any effect was observed. Since these experiments were performed at living polymer concentrations of about 3 and 6 × 10^{-5} *M* one would expect, on the basis of the results given in Table II, a decrease in k_{obsd} by about 20%. Although the discrepancy is greater than the experimental error, we do not attribute to it much significance.

---

[6] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, New York, N. Y., 1959.

Table IV

Homopolymerization of 2-Vinylpyridine in THP at 25°. Counterion Na^+

[∿2-VP$^-$,Na$^+$] × 10^5, *M*	[Na$^+$,BPh$_4^-$] × 10^5, *M*	k_{obsd}, M^{-1} sec^{-1}
9.3	0	5030
5.3	0	4650
2.9	0	4600
1.3	0	5430
6.1	23	4580[a]
5.6	8.3	4430[a]
6.8	7.0	4260[b]
6.8	6.5	4740[b]
5.1	4.8	4440[a]
5.4	2.8	4680[a]
6.5	2.5	4240[b]
7.1	1.5	4270[b]
4.8	1.3	5060[a]
7.0	1.1	4350[a]
7.0	0.91	3810(?)[b]
5.1	0.86	4680[a]

[a] Polymer prepared directly in THP from Na$^-$,DD$^-$,Na$^+$. [b] Polymer prepared by replacing THF with THP.

Table V

Homopolymerization of Sodium Poly-2-vinylpyridine in Dioxane at 25°

[LE] × 10^5, *M*	k_{obsd}, M^{-1} sec^{-1}
9.1	3290
7.6	3270
6.6	3950
5.5	3780
4.2	3360
3.9	3590
2.2	3010

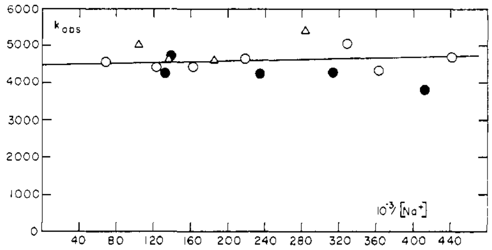

Figure 6. Plot of k_{obsd} *vs.* $1/[LE]^{1/2}$ for the polymerization of ∿(2-VP)$^-$,Na$^+$ proceeding in THP at 25°.

Only a few experiments were performed with cesium polyvinylpyridine in THF. The observed rate constants varied from 1100 to 1500 M^{-1} sec^{-1} at 25° and from 300 to 500 M^{-1} sec^{-1} at 0°. No clear dependence on the concentration of living polymers emerges from these data and, therefore, their analysis in terms of free ions and ion pairs is impractical.

The polymerization was also investigated in THP and in dioxane at 25°. The rate constants determined in the former solvent are listed in Table IV and plotted in Figure 6. Changes in living polymer concentration or the addition of sodium tetraphenylboride had little effect on the results. Apparently the contribution of free ions to the propagation is negligible in THP. The results obtained in dioxane are collected in Table V. Again, no dependence on the concentration of living polymers is observed and the rate constants are intermediate between those observed in THF and those found in THP.

Discussion

Sodium polyvinylpyridine is much less dissociated in THF than sodium polystyrene; the ratio of the respective K_d's is less than 0.01, and the exothermicity of its dissociation is by 5 kcal/mol lower than that of the latter polymer. These facts suggest that some additional binding of Na$^+$ in the ∿VP$^-$,Na$^+$ pair, caused by the lone pair of electrons of the pyridine moiety, adds to the stability of the pair.[3,4] Such an interaction stretches the $^-$C–Na$^+$ bond, increases its dipole moment and therefore increases also the solvation energy of the ion pair. This accounts for the decrease in the exothermicity of the dissociation.

Polymer possessing only one pyridine unit, *i.e.*, ∿S···S·VP$^-$,Na$^+$ is more dissociated than the homopolymer (K_d is greater by a factor of 6). Apparently, even the penultimate pyridine moiety (or perhaps one preceeding it) contributes to the binding of Na$^+$. Because such an intramolecular interaction replaces solvent molecule by pyridine moiety, it decreases the dissociation constant primarily by decreasing the entropy of dissociation. However, this affects only slightly the heat of the reaction.

Inspection of Table III reveals that the homopropagation constant, k_-, of the free living poly-2-vinylpyridine anions in THF is comparable to that of living polystyrene. Although vinylpyridine is a much more reactive monomer in anionic polymerization than styrene,[7] this need not be reflected in the magnitude of the homopropagation constant;[8] the gradation in reactivities is deduced from the copolymerization data.

In contradistinction to the behavior of free ions, the ∿(2-VP)$^-$,Na$^+$ ion pairs appears to be much more reactive than the ∿S$^-$,Na$^+$ pair. For example, at 25° the $k_\pm$ of the latter is 3–6 M^{-1} sec^{-1} in dioxane,[9,10] about 12 M^{-1} sec^{-1} in THP,[11] and still only 80 M^{-1} sec^{-1} in THF,[2] whereas the corresponding rate constants of ∿(2-VP)$^-$,Na$^+$ are 3000–4000 M^{-1} sec^{-1}, 4200–5000 M^{-1} sec^{-1}, and about 2100 M^{-1} sec^{-1}, respectively. It was shown[2] that the low $k_\pm$ rate constants observed in the propagation of ∿S$^-$,Na$^+$ should be attributed to the tight (contact) ion pairs, whereas the loose pairs, characterized by larger interionic distances, are much more reactive, *e.g.*, $k_\pm$ for solvent separated ∿S$^-$,Na$^+$ in THF is as high as 20,000–30,000 M^{-1} sec^{-1} at 25°. It is probable, therefore, that the ∿(2-VP)$^-$,Na$^+$ ion pairs are also "loose," even in media of low solvating power, due to the intramolecular interaction of Na$^+$ with the lone electron pairs of nitrogen.

Comparison of the loose ion pairs with the tight

---

(7) M. Shima, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 1306 (1963).

(8) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957.

(9) G. Allen, G. Gee, and C. Stretch, *J. Polym. Sci.*, **48**, 189 (1960).

(10) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 624 (1965).

(11) M. van Beylen, M. Fisher, J. Smid, and M. Szwarc, *Macromolecules*, **2**, 575 (1969).

ones raises the interesting question of what is the cause of their enhanced reactivity in a propagation process. Two factors should be considered. In the course of addition the cation has to be transferred from the terminal carbanion to the new negative center formed by the addition of monomer. This requires a partial dissociation of the cation which is more facile for the loose than for the tight pair, provided the solvation is not intramolecular. Alternatively, the higher reactivity of the loose pair may arise from the increase in its dipole.

It seems that the latter factor is more important in determining the reactivity of ion pairs. The transfer of Na$^+$ ion is easier even in the "tight" $\sim$S$^-$,Na$^+$ ion pair than in the "stretched" $\sim$VP$^-$,Na$^+$ pair; this is evident when the relevant dissociation processes are compared. Nevertheless, the latter is much more reactive than the former. We do not imply, however, that the facile dissociation of ion pairs does not contribute to their reactivity. Quite to the contrary, this is still a factor which enhances the reactivity of a pair, other things being equal. Indeed, the ease of dissociation may be responsible for the higher reactivity of *solvent separated* $\sim$S$^-$,Na$^+$ in THF when compared with the "stretched" $\sim$(2-VP)$^-$,Na$^+$.

The activation energy of propagation appears to be similar for the free $\sim$(2-VP)$^-$ anion and for the $\sim$(2-VP)$^-$,Na$^+$ ion pairs, about 7–8 kcal/mol. It is interesting to note the same relation in the living polystyrene system; the activation energy of propagation of the free $\sim$S$^-$ ion is about 5–6 kcal/mol and that of the loose $\sim$S$^-$,Na$^+$ ion pair in THF was deduced to be also about 6 kcal/mol. The significance of this relation cannot yet be evaluated.

The effect of solvent upon the propagation constant, $k_\pm$, of $\sim$(2-VP)$^-$,Na$^+$ calls for comments. It may appear surprising that the $k_\pm$ is greater in THP and dioxane than in THF. However, the relatively high reactivity of $\sim$S$^-$,Na$^+$ in THF, and even more so in DME,[12] when compared with its reactivity in dioxane or THP results from the substantial contribution of the loose pairs to the overall reactivity. In THP or dioxane we observed the growth of tight pairs only whereas the reactivity of tight pairs in THF is not known. On the other hand, in the $\sim$VP$^-$,Na$^+$ system we are concerned with the reactivities of "stretched" ion pairs which may be only slightly influenced by the solvent. The relatively high reactivity of the $\sim$(2-VP)$^-$,Cs$^+$, when compared with the sodium salt, becomes plausible when the idea of internal solvation by the polymer is accepted.

Finally, it should be remarked that similar effects arising from the intramolecular solvation of the cation have been observed recently in the system living poly-*o*-methoxystyrene.[13] Here again the favorable location of the *o*-methoxy group makes possible the intramolecular solvation of the cation and the reactivity of this polymer is indeed much higher than that of the living polymer derived from the *p*-methoxy styrene.

Acknowledgment. We gratefully acknowledge the financial support of this investigation to the National Science Foundation and to the Petroleum Research Fund administered by the American Chemical Society.

---

(12) T. Shimomura, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 5743 (1967).

(13) J. Geerts, M. van Beylen, and G. Smets, *J. Polym. Sci., Part A-1*, 2859 (1969).

Nuclear Magnetic Resonance Spectra of a Isobutylene–Chlorotrifluoroethylene Copolymer

Kenkichi Ishigure, Yoneho Tabata, and Keichi Oshima

Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan.

Received June 23, 1969

ABSTRACT: High-resolution nmr spectra were measured at 94 MHz (100 MHz) and 56.4 MHz for both ^{19}F and ^{1}H nuclei of chlorotrifluoroethylene–iosbutylene copolymers polymerized by γ irradiation. It was concluded from the nmr spectra that the copolymers have completely alternating structure and that a propagating isobutylene radical adds to chlorotrifluoroethylene monomer on the carbon atom with two fluorine substituents in the polymerization reaction. The CF$_2$ resonance was found to be an AB-type quartet, being affected by the nearest neighboring asymmetric center of –CFCl–. The methyl resonance, a doublet with equal intensity, seems to suggest the possibility of the stereospecific structure of the polymers.

Many successful results have been obtained in determining the microstructure of polymers and copolymers by means of nuclear magnetic resonance (nmr) measurements. Most of them, however, are concerned with proton spectra of polymers and there are few investigations of the structure of polymers by fluorine spectra.[1-3]

It has been reported by the authors that several kinds of fluorine-containing polymers can be obtained by copolymerization induced by ionizing radiation.[4] The structure of isobutylene (IB)–chlorotrifluoro-

---

(1) R. C. Ferguson, *J. Amer. Chem. Soc.*, **82**, 2416 (1960).

(2) G. V. D. Tiers and F. A. Bovey, *J. Polym. Sci., Part A-1*, 833 (1963).

(3) C. W. Wilson, III, and E. R. Santee, Jr., *ibid., Part C*, 8, 97 (1965).

(4) Y. Tabata, K. Ishigure, H. Shibano, K. Oshima, and H. Sobue, Proceedings of Conference on Industrial Uses of Large Radiation Sources, Vol. 1, 1963, p 179.