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Syntheses and Reactions of Functional Polymers. XL. Enhanced Reactivity of Poly(vinyl chloride) by Neighboring-Group Participation of the *N*,*N*-Disubstituted Dithiocarbamate Function[*1]

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In order to demonstrate that neighboring-group participation of the *N*,*N*-disubstituted dithiocarbamate function is involved in the substitution reaction of poly (vinyl chloride) (PVC) with the dithiocarbamate anion, the rates of reactions of PVC and the copolymer (vinyl chloride-*S*-vinyl *N*,*N*-diethyldithiocarbamate) with $^{-}$SCS-NEt$_2$ were compared under the same conditions. These polymer reactions were undertaken in dimethylformamide or tetrahydrofuran at 45°C. The rate enhancements with the copolymer were observed in both solvents. From these observations, it was concluded that the chloromethylene groups in PVC neighboring the dithiocarbamate function were activated toward the nucleophile *via* neighboring-group participation. This is the first time that neighboring-group participation involving the polymer main chain might be observed in the polymer reaction. The difference in reaction mechanism between the polymer reaction and the model reaction was discussed.

It is well-known that poly(vinyl chloride) (PVC) is more unsusceptible to nucleophilic substitution (S_N) reactions and more readily eliminates hydrogen chloride, as compared with alkyl chlorides. For that reason, chemical modifications of PVC have been subjected to restriction.

During the course of our studies on preparations of photosensitive polymers containing the dithiocarbamate function by polymer reactions, it was found that PVC reacted readily with dithiocarbamate anions in dimethylformamide (DMF) at 40—50°C without elimination of hydrogen chloride.[1] The remarkable reactivity of PVC under mild conditions might be due to three factors: (i) the enhanced electrophilicity of PVC by the solvation with DMF,[2] (ii) the large nucleophilicity of the dithiocarbamate anion[3] and (iii) enhancement of the nucleophilicity by DMF.[4]

On the other hand, we have reported that neighboring-group participation of the *N*,*N*-disubstituted dithiocarbamate function is involved through the intermediacy of the isolatable anchimeric cation[*3] in the reactions of 1,2-dichloroethane[5] and 1,3-dichloropropane (a model compound for PVC)[6] with the dithiocarmate anion, *e. g.*, as shown in Scheme 1.

The present work was undertaken in order to prove that neighboring-group participation of the

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[1] a) M. Okawara, K. Morishita and E. Imoto, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **69**, 761 (1966); b) T. Nakagawa, Y. Taniguchi and M. Okawara, *ibid.*, **70**, 2382 (1967). For other types of photosensitive polymers containing the dithiocarbamate function, also see M. Okawara and coworkers, *ibid.*, **66**, 1383 (1963); **69**, 766 (1966).

[2] S. Yoneda and co-workers [*ibid.*, **68**, 1074, 1077 (1965)] have reported that the electrophilicities of alkyl halides are enhanced by the complex formation with DMF.

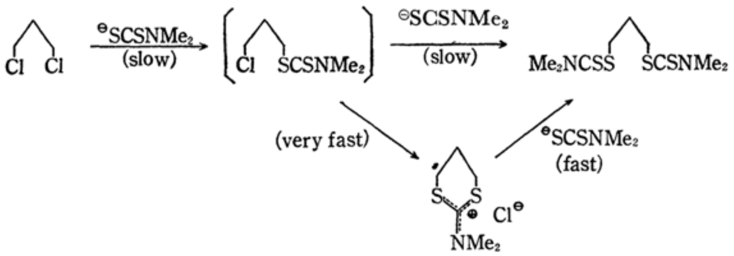
[3] Dithiocarbamate anions are ranked with the strongest nucleophiles in aqueous solutions: R. E. Davis, "Survey of Progress in Chemistry," Vol. 2, ed. by A. Scott, Academic Press Inc., New York, N. Y. (1964), p. 189; R. E. Davis, H. Nakshbendi and A. Ohno, *J. Org. Chem.*, **31**, 2702 (1966).

[4] Rate enhancements of the S_N reactions in dipolar aprotic solvents such as DMF have been reported in many literatures. For reviews on this subject, see A. J. Parker, *Quart. Revs.*, **16**, 163 (1962); "Advances in Physical Organic Chemistry," Vol. 5, ed. by V. Gold, Academic Press Inc., New York, N. Y. (1967), p. 173.

[*3] The word "anchimeric cation" stands for the cyclic carbonium ion formed *via* the intramolecular S_N reaction involving the neighboring group, such as 2-dimethylamino-1,3-dithian-2-ylium ion in Scheme 1.

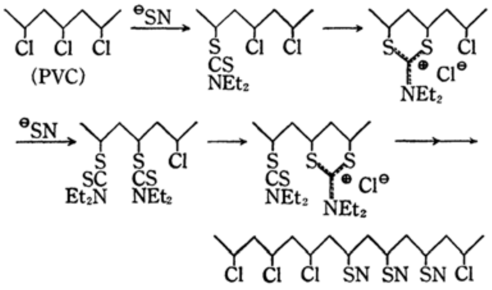
[5] T. Nakai, Y. Ueno and M. Okawara, *Tetrahedron Letters*, **1967**, 3831.

[6] T. Nakai, Y. Ueno and M. Okawara, Abstracts of papers presented at the 18th Symposium on Organic Reaction Mechanisms, Kyoto, October, 1967, p. 77.



Scheme 1

dithiocarbamate function is certainly involved in the reaction of PVC with *N*,*N*-diethyldithiocarbamate anion (⁻SN). Assuming that the concept of neighboring-group participation might be applied into the polymer reaction of PVC with ⁻SN, the reaction should proceed as shown in Scheme 2 to result in the formation of the polymer containing the block-type structure (I).

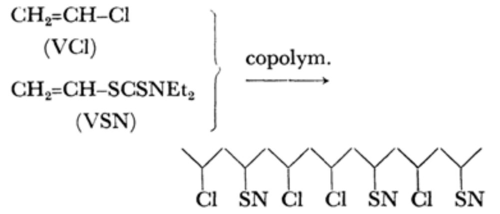


(I)

(SN=SCSNEt$_2$)

Scheme 2

On the other hand, the copolymer from vinyl chloride (VCl) and *S*-vinyl *N*,*N*-diethyldithiocarbamate (VSN) should be of the random structure as given by the formula (II).



(II)

Consequently, it can be said that the polymer (II) apparently contains more chloromethylene (–CHCl–) groups neighboring the dithiocarbamate function than the polymer (I) does. Thus, in order to demonstrate that the neighboring group participates in the polymer reaction, we attempted to compare the rate of reaction of the polymer (I) and ⁻SN with that of the polymer (II) under the same reaction conditions.

Results

Reactions of PVC with Sodium *N*,*N*-Diethyldithiocarbamate (NaSN). Reactions of PVC with NaSN (initial molar ratio 2 : 1) were carried out in DMF or tetrahydrofuran (THF) at 45°C. The reaction was followed by the sulfur analysis of the resulting polymer precipitated after a given interval. The results obtained are shown in Table 1. As shown in Fig. 1, the reaction fitted in a second-order rate equation (the rate constant= 2.78×10^{-6} mol^{-1}·l·sec^{-1}). It may be noted that the rate of reaction in DMF is much larger than that in THF. The fact indicates that the three factors described above have a serious influence on the rate of reaction.

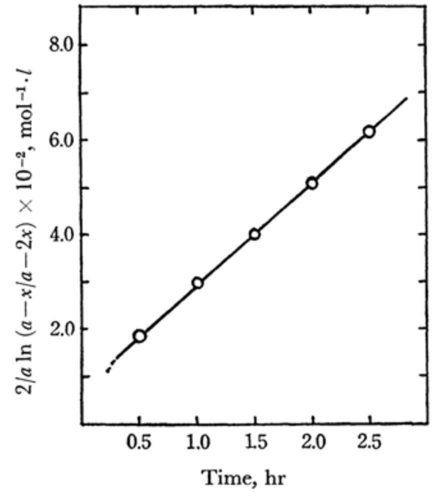


Fig. 1. Second-order rate plot for the reaction of PVC with NaSN in DMF at 45°C.

Reactions of the Copolymer (VCl-VSN) with NaSN. *S*-Vinyl *N*,*N*-diethyldithiocarbamate (VSN) was prepared by the vacuum pyrolysis of ethylene bis(*N*,*N*-diethyldithiocarbamate).[7] The copolymerization of VCl with VSN was undertaken in bulk at 45°C using *a*,*a*′-azobisisobutyronitrile

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[7] T. Nakai, K. Shioya and M. Okawara, *Makromol. Chem.*, **108**, 95 (1967).

TABLE 1. REACTIONS OF PVC WITH NaSN

PVC ($\bar{P}$=400) 7.5 g (0.12 mol); NaSN 10.3 g (0.06 mol)
Solvent 170 m*l*; Reaction temp. 45±0.5°C

Solvent	Time hr	Resulting polymers: Sulfur content %*	Resulting polymers: Concn. of VSN, mol%
DMF	0.5	5.75	6.23
	1.0	8.23±0.02	9.37
	1.5	9.81±0.01	11.5
	2.0	11.21±0.02	13.6
	2.5	12.25±0.03	15.2
THF	1.5	0.73±0.04	0.721
	2.0	0.84±0.03	0.830
	2.5	1.02±0.04	1.01

* An average and a variation of values obtained by two analyses.

(AIBN) as an initiator. The reactivity ratio of these monomers, r_{VCl} and r_{VSN}, were tentatively calculated using the Q,e values obtained from the respective copolymerization with styrene (VCl Q=0.044, e=+0.20[8]; VSN Q=0.45, e=−1.54[7]). The ratio r_{VCl} and r_{VSN} obtained were 0.069 and 1.426, respectively, indicating that VCl is less reactive than VSN. Thus, in order to prepare the random copolymer such as the formula (II), VSN was copolymerized with VCl from a low range of feed compositions. All copolymers were obtained in the form of solid. The experimental data are shown in Table 2. Concentrations of VSN

TABLE 2. COPOLYMERIZATION OF VCl WITH VSN
Polym. temp. 45±0.5°C; AIBN 0.130 g

VCl g	VSN g	Time hr	Conv. %	Copolymers: Sulfur content* %	Copolymers: Concn. of VSN mol%
11.50	0.54	50	32.3	2.28±0.01	2.25
11.70	0.86	33	22.3	4.44±0.03	4.70
12.69	1.15	48	21.1	5.79±0.00	6.40
12.64	1.58	72	28.1	6.06±0.03	6.65
11.96	1.61	72	30.7	6.46±0.01	7.10
11.31	1.74	33	19.8	9.40±0.02	10.3

* An average and a variation of values obtained by two analyses.

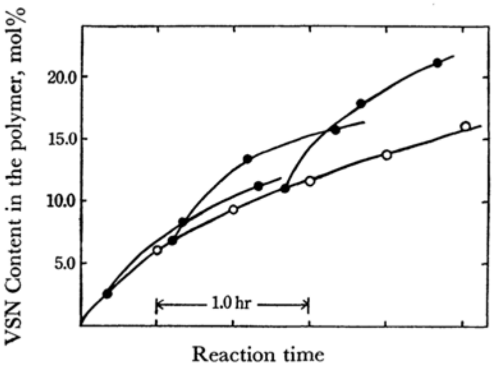

Fig. 2. Reactions of PVC and copolymers with NaSN in DMF.
○: PVC ●: Copolymer

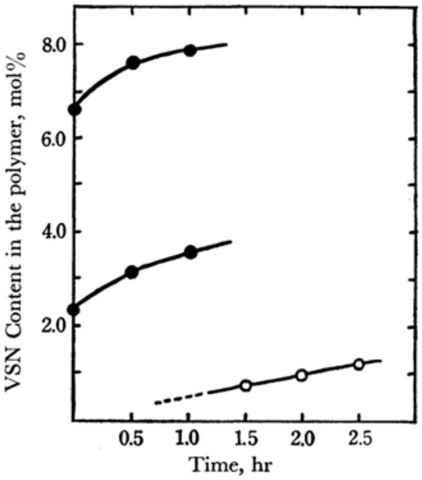

Fig. 3. Reactions of PVC and copolymers with NaSN in THF.
○; PVC ●; Copolymer

TABLE 3. REACTIONS OF COPOLYMERS WITH NaSN

Reaction temp. 45±0.5°C
Initial molar ratio; (VCl in the copolymer+added NaCl): (VSN in the copolymer+added NaSN) =2 : 1

Solvent	Reactant copolymer[a] Concn. of VSN mol%	Time hr	Resulting copolymer: Sulfur content %[b]	Resulting copolymer: Concn. of VSN mol%
DMF	2.32	0.5	7.28±0.01	8.16
		1.0	9.34±0.03	10.9
	4.70	1.0	10.43±0.05	13.3
	6.65	0.5	10.42±0.01	13.3
		1.0	12.24±0.02	15.3
	11.0	0.5	13.95±0.03	17.4
		1.0	15.64±0.04	21.1
THF	2.32	0.5	3.05±0.01	3.15
		1.0	3.24±0.00	3.36
	6.65	0.5	6.99±0.02	7.79
		1.0	7.05±0.02	7.87

a) See Table 2
b) An average and a variation of values obtained by two analyses.

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[8] L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).

in the copolymers were evaluated by sulfur analyses.

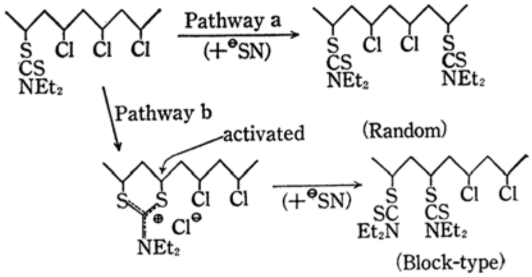
Next, reactions of these copolymers with NaSN were undertaken in DMF or THF under the same conditions as the reaction of PVC described above. Then, in order to compare exactly reactivities of the copolymer and PVC containing the same amount of VSN as the copolymer, the same molar amount of sodium chloride as that of VSN in the copolymer was added to the reactant mixture and the initial molar ratio (VCl in the copolymer+added NaCl)/(VSN in the copolymer+added NaSN) was adjusted to two in all cases. The VSN content of the resulting copolymer precipitated after a given interval was evaluated by the sulfur determination. The results obtained are given in Table 3. The plots of the VSN content in the resulting copolymers against the time are shown in Figs. 2 and 3, together with data for the reaction of PVC as references.

Discussion

Figure 2 shows important facts: (i) the rate enhancement[*4] with the copolymer was clearly observed as compared with PVC containing the same concentration of VSN as the copolymer and (ii) the rate enhancement with the copolymer increased with the concentration of VSN in the copolymer. These facts lead substantially to the reasonable conclusion that participation of the neighboring dithiocarbamate function is no doubt involved in these polymer reactions, that is, the chloromethylene groups neighboring the dithiocarbamate function are activated toward the dithiocarbamate anion, as described in Scheme 2. These facts also indicate that the polymer from PVC and $^-$SN contains considerably the block-type structure such as the formula (I). This is the first time that neighboring-group participation involving the polymer main chain might be observed in the polymer reaction. The neighboring-group effects in polymer reactions reported so far all involve the polymer side chains. This method for activating PVC may further provide a possibility of a variety of chemical modifications of PVC *via* the S_N reaction with other nucleophiles which resist reaction with PVC itself. We are studying the reaction of the copolymer(VCl-VSN) with other nucleophiles.

Contrany to expectation the solvent effect on the rate enhancement with the copolymer was not particularly predominant (compare Figs. 2 and 3). This finding is in direct contrast to the observation that in the reaction of 1,2-dichloroethane with *N*,*N*-dimethyldithiocarbamate anion, neighboring-group participation of the dithiocarbamate function in THF is about two hundred times as large as that in DMF.[5] Taking it into consideration that the large solvent effect was observed on the rate of reaction of PVC with $^-$SN, this fact indicates that the normal S_N2 reaction involving no neighboring-group participation simultaneously occurs in the polymer reactions and that, in contrast to reactions of 1,2-dichloroethane and 1,3-dichloropropane described above, the intramolecular cyclization involving the neighboring dithiocarbamate function is slow for the polymer reaction.

In short, these polymer reactions consist of both the normal S_N2 reaction (pathway a) and the intramolecular cyclization followed by the S_N reaction (pathway b) giving a random polymer and block-type polymer respectively, as shown below.



Scheme 3. Copolymer or PVC containig the SN function.

In all cases kinetical observation leads to the conclusion that the S_N reaction involving neighboring-group participation (pathway b) certainly occurs in the polymer reaction.

Experimental

Materials. Commercial NaSN was washed several times with chloroform and then dried *in vacuo*. This salt contains two molecules of coordinated water.[9] Commercial PVC (P=400) was purified by reprecipitating twice (DMF-MeOH). *S*-Vinyl *N*,*N*-diethyldithiocarbamate (VSN) was prepared by the vacuum pyrolysis of ethylene bis(*N*,*N*-diethyldithiocarbamate)[7] and then twice distilled at a reduced pressure (yield 95%); bp 93—94°C/1 mmHg, n_D 1.588 (27°C).

The solvents employed were purified by the usual methods.

Copolymerization Procedure. Commercial VCl was purified as follows: VCl was transferred into a flask cooled in a Dry Ice mixture from a cylinder through

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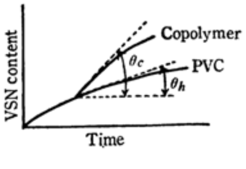
[*4] The rate enhancement with the copolymer is related to the ratio $\tan\theta_c/\tan\theta_h$ which was more than one, as illustrated below.



[9] T. Nakai and M. Okawara, This Bulletin, **41**, 707 (1968).

a 10% aqueous solution of sodium hydroxide and a soda lime column. Using the usual vacuum system, VCl was further distilled through a soda lime column and then a given amount of purified VCl was condensed into a hard-glass tube of approximately 150 m*l* capacity containing given amounts of VSN and AIBN. The tube was carefully sealed and then immersed into a thermostat maintained at 45±0.5°C. After a given interval, the tube was removed from the thermostat and opened at −78°C. The reaction mixture was poured into a large amount of methanol giving a slightly yellowish precipitate. The copolymer was filtered and dried *in vacuo*. The copolymer was purified by reprecipitation (DMF-MeOH) and then completely dried *in vacuo*. The concentration of VSN in the copolymer was evaluated by sulfur determinations. The experimental results obtained are summarized in Table 2.

Polymer Reaction Procedure. The reaction of PVC with NaSN was undertaken as follows: a solution of 6.30 g (0.10 mol) of PVC and 8.60 g (0.05 mol) of NaSN in 100 m*l* of DMF was stirred in the thermostat maintained at 45±0.5°C. After a given interval, 25 m*l* of the reaction mixture was pippetted out and then poured into approximately 100 m*l* of methanol giving a white precipitate. The resulting polymer was purified by reprecipitation (DMF-MeOH) and dried *in vacuo*. The degree of substitution, that is, the concentration of VSN in the resulting polymer, was evaluated by two sulfur determinations. The experimental results obtained are summarized in Table 1. Infrared spectra of the resulting polymers exhibited no absorption bands due to the carbon-carbon double bond, indicating that no elimination of hydrogen chloride occurred during the reaction.

The reaction of the copolymer prepared above with NaSN was carried out under the same conditions as those of PVC. For example, a solution of 1.00 g of the copolymer (sulfur content 6.06%), 0.055 g of NaCl and 1.10 g of NaSN in 14.3 m*l* of DMF was stirred at 45°C. After a given interval, 7 m*l* of the reaction mixture was poured into methanol to give a slightly yellowish precipitate. The content of VSN in the resulting copolymer was evaluated by sulfur determinations. The results obtained are given in Table 3.

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