Nonclassical Urea Oligomers. 2. Solvation-Assisted Polymerization of 1-(*N*-Phenylcarbamoyl)aziridine by S=O or P=O Containing Compounds and Specific Absorption of the Compounds to the Polymer

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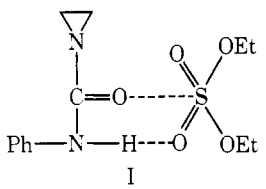
ABSTRACT: Control of the reaction course of 1-(*N*-phenylcarbamoyl)aziridine (NPCA) by solvation-assisted mechanism was observed for a variety of S=O or P=O containing compounds: diethyl sulfate, ethyl *p*-toluenesulfonate, ethyl *p*-toluenesulfinate, dimethyl sulfoxide, diphenyl sulfoxide, dimethyl sulfone, diphenyl sulfone, tetramethylene sulfone, triethyl phosphine oxide, triphenyl phosphine oxide, diethyl ethanephosphonate, and triethyl phosphate. The poly(NPCA) obtained in the presence of a S=O or P=O compound absorbs the S=O or P=O compound in different amounts. The affinity was estimated by reabsorption studies with the "freed polymer". The correlation diagram obtained by plotting catalyst activity of the S=O or P=O compound vs. affinity for the poly(NPCA) indicated these S=O and P=O compounds can be classified into three types: (1) S=O compounds in which both catalyst activity and affinity are in the reverse order of hydrogen bond accepting nature. (2) S=O compounds in which catalyst activity is reverse to hydrogen bond accepting property, whereas the affinity for the poly(NPCA) is parallel to the factor. (3) P=O compounds which behave similarly as in case (2). Monomer NPCA does not form stable molecular complex with the S=O or P=O compound. On combining with IR studies, however, solvation of the S=O and P=O compounds to the monomer NPCA is strongly suggested to involve such an interaction as type I to form solvated monomer by dissociating the monomer aggregation. The solvated monomer is shown to be more active than the aggregated state and simultaneously it prevents the reaction sites responsible for side reaction, i.e., isomerizations. Absorption specificity of the poly(NPCA) for the S=O and P=O compounds is of value because the poly(NPCA) is a non-cross-linked oligomeric ($\overline{DP} \sim 8$) compound.

We have found[2] that diethyl sulfate specifically controls the reaction course of 1-(*N*-phenylcarbamoyl)aziridine and its analogues to form polymers (DP ~ 8) of the type $(CH_2CH_2N(CONHPh))_n$, without forming isomerization products, N,N-disubstituted piperazine, and polymer of poly(imino ether) type. And strong affinity of diethyl sulfate for the polymer was observed.[2] Our postulation about the role of the diethyl sulfate in controlling the polymerization was that it plays as an initiator and a solvating reagent which solvates the aziridine monomer by interacting with both of the –NH– and C=O groups to result in a shielding effect at the sites responsible for isomerization into oxazoline and imidazolidinone derivatives. The interaction postulated is one, for example, as type I.



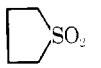
I

According to the postulation, it seems likely that a variety of compounds containing S=O or P=O group can interact similarly with the monomer to cause similar solvation-assisted effects in the polymerization reaction. Further, they may show affinities for the polymer. This work is concerned with the testing of these problems by varying the nature of the S=O and P=O compounds. The results indicated that these expectations were essentially consistent, and by combining with IR studies it was suggested that solvation of a S=O or P=O compound dissociates the monomer aggregation into an activated monomer of type I.

Absorption experiments of the S=O and P=O compounds to the "freed polymer" (cf. later section) demonstrated characteristic affinities of these compounds. This specificity of the affinity may be due to alteration of the polymer conformation in the presence of the guest molecules.

Results and Discussion

Behavior of S=O Compounds in Polymerization Reaction. The S=O compounds used here include aliphatic sulfate (diethyl sulfate, Et_2SO_4), aromatic sulfonate (ethyl *p*-toluenesulfonate, *p*-tolyl-SO_2-OEt), aromatic sulfinate (ethyl *p*-toluenesulfinate, *p*-tolyl-SO-OEt), aliphatic sulfoxide (dimethyl sulfoxide, Me_2SO), aromatic sulfoxide (diphenyl sulfoxide, Ph_2SO), aliphatic sulphone (dimethyl sulfone, Me_2SO_2), aromatic sulfone (diphenyl sulfone, Ph_2SO_2), and cyclic sulfone (tetramethylene sulfone,



The polymerization behaviors of 1-(*N*-phenylcarbamoyl)-aziridine (NPCA) in the presence of these S=O compounds were compared under the same conditions, i.e., at 60 °C in ethyl acetate.

Among the S=O compounds used, only two (Et_2SO_4 and *p*-tolyl-SO_2-OEt) were catalytically active without cocatalyst. These are restricted to esters of strong acids which can librate ethyl cations. Other S=O compounds were inactive by themselves but became active when a small amount (4 mol % of monomer) of Et_2SO_4 was added as cocatalyst. The amount of the added Et_2SO_4 as cocatalyst was small enough to form a detectable quantity of the polymer in the absence of a S=O compound of almost equimolar amount to the monomer. A proton donor such as *p*-toluenesulfonic acid or benzoic acid can also be used as cocatalyst.

The polymer yields shown in Table I can be used as a measure of the rate of polymerization under the given conditions. The polymers formed in the presence of various S=O compounds were identical in IR and NMR with that obtained with Et_2SO_4, i.e., nonclassical urea type structure[3] having similar molecular weights, $-(CH_2CH_2N(CONHPh))_n-$. The tendencies in the polymerization behaviors of the S=O compounds are: (i) Increasing number of the S–O group increases the rate of polymerization of NPCA. This tendency is almost reverse to the hydrogen bonding accepting property of the S=O compounds but almost parallel to the semi polar nature of the $S^{\delta+}=O^{\delta-}$ bond. (ii) Increasing aromatic substitution in the S=O compounds decreases the rate of polymerization. This tendency is parallel to the steric effect on the phenyl group and also to the decrease in the hydrogen bonding accepting property.

Table I
Polymerization[a] of 1-(*N*-Phenylcarbamoyl)aziridine in the Presence of Several S=O Containing Compounds

No.	S=O compd	Polymer yield, % S=O compd alone	S=O compd + 4 mol % Et_2SO_4[b]	S=O compd + 4 mol % *p*-TsOH[b]
1	$(EtO)_2SO_2$	45–60		
2	*p*-Tolyl-SO_2OEt	30		
3	*p*-Tolyl-SO-OEt	0	35	12
4		Trace	24	33
5	Me_2SO	0	23	33
6	Me_2SO_2	0	15	29
7	Ph_2SO	0	22	10
8	Ph_2SO_2	0	31	36

[a] Polymerization conditions: monomer, 0.0020 mol; S=O compd, 1 mol/mol of monomer; solvent, ethyl acetate, 10 mL; temperature, 60 °C; time, 23 days. [b] No polymer was obtained with Et_2SO_4 or *p*-TsOH alone in the concentration of 4 mol % of the monomer.

Table II
Polymerization[a] of 1-(*N*-Phenylcarbamoyl)aziridine with Several P=O Containing Compounds

No.	P=O compd	Polymer yield, % P=O compd alone	P=O compd + 4 mol % of Et_2SO_4[b]
9	$Et_3P=O$	0	3.7
10	$Ph_3P=O$	0	5.4
11	$(EtO)_2P(O)Et$	0	5.9
12	$(EtO)_3P=O$	Trace	19.4
13	$(PhO)_3P=O$	10	12.5

[a] Polymerization conditions: monomer, 0.0020 mol; P=O compd, 1 mol/mol of monomer; solvent, ethyl acetate 10 mL; temperature, 60 °C; time, 23 days. [b] No polymer was obtained with Et_2SO_4 alone in the concentration of 4 mol % of the monomer.

Behavior of P=O Compounds in Polymerization Reaction. The P=O compounds used in this study are: aliphatic phosphine oxide (triethyl phosphine oxide, $Et_3P=O$), aromatic phosphine oxide (triphenyl phosphine oxide, $Ph_3P=O$), aliphatic ethanephosphonate (diethyl ethanephosphonate, $(EtO)_2P(O)Et$), aliphatic phosphate (triethyl phosphate, $(EtO)_3P=O$), and aromatic phosphate (triphenyl phosphate, $(PhO)_3P=O$).

The activity of the P=O compounds was weaker than that of the corresponding S=O compounds, but the solvating effects were clearly observed for all of these P=O compounds when a catalytic amount of Et_2SO_4 was present (Table II). Triphenyl phosphate was the only compound which could initiate the polymerization without cocatalyst. This is again an ester of a relatively strong acid of phosphoric acid. The tendency of the initiating activity in the presence of Et_2SO_4 cocatalyst was almost reverse to the hydrogen bonding accepting property of the P=O compounds. Lower polymer yields for the use of the P=O compounds compared with the S=O compounds may be due to weaker contribution of P–O semipolar interaction.

The polymers formed in the presence of these P=O compounds were identical with those obtained with Et_2SO_4 when freed from the absorbed P=O compounds.

Affinity with Polymer. The polymers obtained in the presence of the S=O and P=O compounds contained the corresponding S=O and P=O compound after being washed with ethyl acetate (we denote these as "washed polymer" according to the case of the Et_2SO_4 system[2]). As a typical example, IR spectra (Figure 1) of the polymers obtained with *p*-tolyl-SO-OEt and $(PhO)_3P=O$ are compared with those obtained with Et_2SO_4 and its Amberlite-treated "freed polymer".[2] Identity of the CO–NH frequencies, and therefore polymer structure, of the three polymers is apparent. In addition, it is also clear that the "washed polymers" obtained with *p*-tolyl-SO-OEt and $(PhO)_3P=O$ contain different amounts of these compounds.

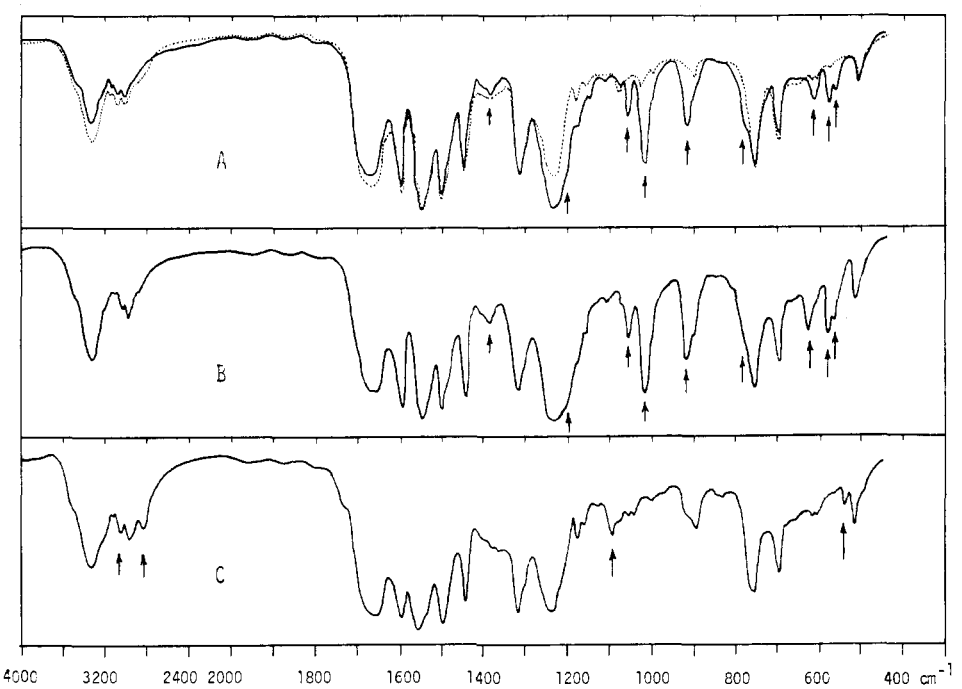


Figure 1. IR spectra of "washed" and "freed" poly(NPCA)s. A: Poly(NPCA) obtained with Et_2SO_4: (—) "washed polymer", and (- - -) "freed polymer". B: Poly(NPCA) obtained with *p*-tolyl-SO-OEt. C: Poly(NPCA) obtained with $(PhO)_3P=O$. Arrows indicate the bands due to absorbed Et_2SO_4, *p*-tolyl-SO-OEt, and $(PhO)_3P=O$ compounds, respectively. The spectra were recorded for KBr disks.

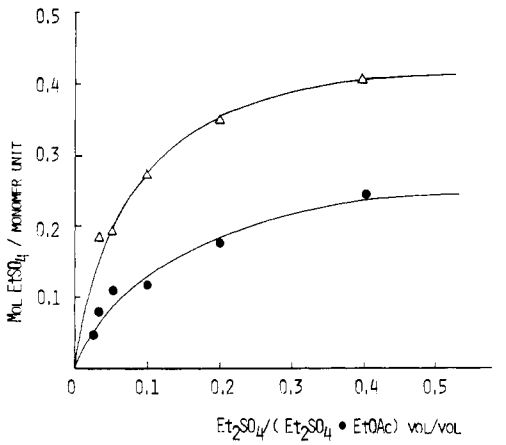


Figure 2. Resorption of Et_2SO_4 to the "freed" poly(NPCA) as a function of Et_2SO_4 concentration: (-●-) at 3.5 °C and (△) at 60 °C. Resorption conditions: "freed" polymer, 0.0020 mol (one monomer unit in the polymer was regarded as 1 mol); medium, ethyl acetate 10 mL; state, powdery suspension; time, 8 days. The reabsorbed mole of Et_2SO_4 was determined from the S content (by elemental analysis) in the resulted polymer.

For the study of polymer affinity, the "freed polymer" [which was obtained from the polymer prepared in the presence of Et_2SO_4 and then the Et_2SO_4 absorbed was removed by Amberlite treatment according to the method described in the preceding paper[2] (S = 0.09%)] was suspended in ethyl acetate containing an equimolar amount (per monomeric unit in the polymer chain) of S=O or P=O compound for 8 days. And the reabsorbed amount of the S=O or P=O compound was estimated from elemental analysis of the resulted polymer.

Figure 2 shows the amounts of Et_2SO_4 reabsorbed as a function of Et_2SO_4 concentration and temperature. The reabsorbed amount increases with the concentration of Et_2SO_4 until the concentration reaches ca. 20%. However, at higher concentrations saturation is observed in the reabsorbed amount of Et_2SO_4. The reabsorption behavior significantly depends upon temperature, i.e., it increases with the temperature elevation, and these temperature dependencies in reabsorption are similar to those observed in the polymerization behavior.

The amounts of variety of S=O and P=O compounds reabsorbed at 60 °C at saturation are tabulated in Table III, in which the values are shown by the number of monomer units (N^*) in the polymer chain required for absorption of one molecule of the S=O or P=O compound. There was a remarkable difference in the N^* values, indicating that the polymer has selective affinity for the different types of S=O and P=O compounds. It is clear that the affinities for the S=O compounds are generally higher than those of the P=O compounds. The average number of polymer chains and the absorbed compounds estimated assuming that the average DP of the polymer is 8[2] are tabulated in Table IV. Such a specificity in affinity is probably assisted by the specific variation of polymer conformation upon absorption of a given S=O or P=O compound. This kind of variation of the polymer conformation with the guest molecules seems highly important, because this phenomenon may be correlated with essential functionality in the recepting system, though our system is not involved in the biological tissues.

The basis of the variation of conformation in the polymer chain can be suggested from the relatively rigid nature of the polyethylenimine backbone and urea-type side chain, viz., Litt and co-workers[4] have shown that poly(N-acylaziridine) has a regularly ordered structure in which the COR side chains constitute cavities of 6.4–6.8 Å diameter. Further supports of the conformational regidity of the polyethylenimine backbone may be suggested from the results of catalysis by optically active polyethylenimines for asymmetric synthesis of benzaldehyde cyanohydrin[5] or asymmetric addition reaction of mercaptanes to unsaturated carbonyl compounds.[6] In addition, optically active polyalkylenimines carrying bulky substituents such as the benzoyl group have been shown to exist as regularly helical conformations.[7-9] On considering that the urea-type side group of our polymer, >N–CO–NH–Ph, is rotationally hindered to a considerable extent, the enhancement of the rigidity in the polymer conformation in our case can be reasonable.

Correlation between Catalytic Activity and Affinity for the Polymer. On plotting the catalytic activity of the S=O and P=O compounds shown in Tables I and II against their affinity with the poly(NPCA), we obtained a correlation diagram as illustrated in Figure 3. The diagram is composed

Table III
Resorption[a] of S=O and P=O Compounds into Freed Polymer

Compounds reabsorbed	Analytical value, % S	P	N	N^*[b]
$(EtO)_2SO_2$	3.61		14.55	4.61
p-Tolyl-SOEt	3.18		14.40	5.18
p-Tolyl-SO_2OEt	3.00		14.33	5.51
p-Tolyl-SO-OEt	1.29		15.98	14.2
p-Tolyl-SO_2-Et	1.21		16.06	15.2
	1.15		16.34	16.3
Me_2SO	0.97		16.51	19.5
Me_2SO_2	0.93		16.54	20.4
Ph_2SO	0.65		13.80	24.3
Ph_2SO_2	0.48		16.45	39.2
$Et_3P=O$		0.74	15.44	26.6
$Ph_3P=O$		0.50	15.30	33.8
$(EtO)_2P(O)Et$		0.26	14.90	63.3
$(EtO)_3P=O$		0.12	16.49	151
$(PhO)_3P=O$		0	15.81	∞

[a] Resorption conditions: freed polymer, 0.0020 mol; S=O or P=O compound, 1 mol/mol of freed polymer; medium, ethyl acetate 10 mL, state, suspension; temperature, 60 °C; time, 8 days. [b] Number of monomeric units in the polymer chain required for absorption of one molecule of the S=O or P=O compounds.

Table IV
Estimation of Average Numbers of Polymer Chain and Absorbed Compounds[a]

Compd	Av. No. of polymer chain	Av. No. of absorbed compd
$(EtO)_2SO_2$	1	2
p-Tolyl-SOEt	1	1–2
p-Tolyl-SO_2-OEt	1	1–2
p-Tolyl-SO-OEt	2	1
p-Tolyl-SO_2Et	2	1
	2	1
Me_2SO	2–3 (5)	1 (2)
Me_2SO_2	2–3 (5)	1 (2)
Ph_2SO	3	1
Ph_2SO_2	5	1
$Et_3P=O$	3–4 (7)	1 (2)
$Ph_3P=O$	4	1
$(EtO)_2P(O)Et$	8	1
$(EtO)_3P=O$	20	1
$(PhO)_3P=O$	∞	1

[a] Values are estimated from the N^* (Table III) by assuming that the average degree of polymerization of poly(1-(N-phenylcarbamoyl)aziridine) is 8.

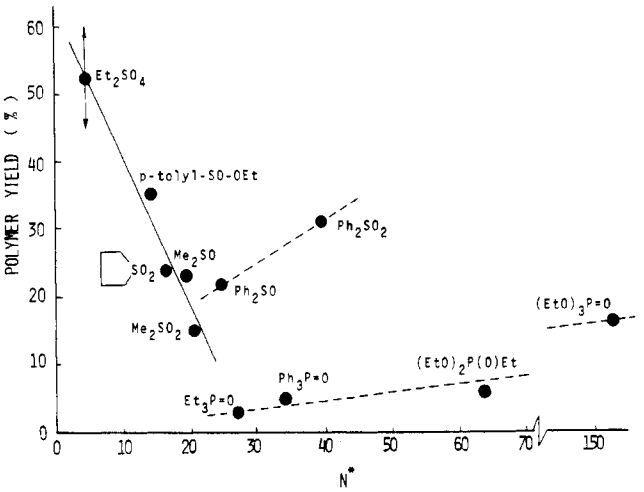


Figure 3. Correlation between catalytic activity of various S=O and P=O compounds and their affinity for poly(NPCA). N^* = the number of monomeric units in the polymer chain required for absorption of one molecule of the S=O or P=O compound. Note that smaller N^* values mean stronger affinity.

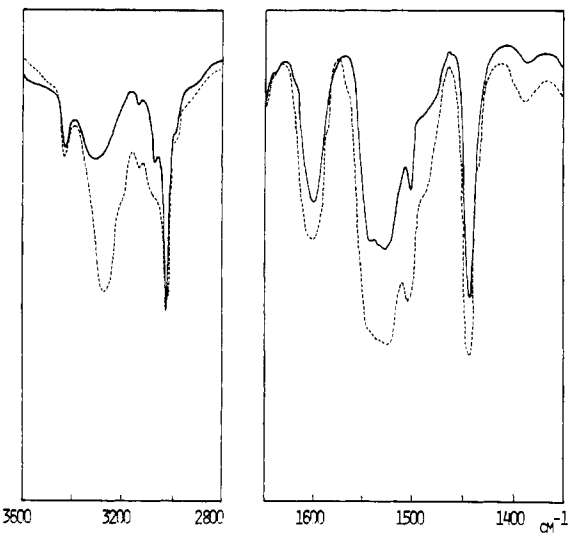


Figure 4. Variation in the IR spectra of NPCA monomer in $CHCl_3$ solutions in the presence and absence of Ph_2SO_2: (- -) NPCA solution (1.0 mol/L), and (—) an equimolar mixture of NPCA (1.0 mol/L) and Ph_2SO_2 (1.0 mol/L) solutions.

of three independent lines. Although the three lines do not rationalize any physicochemical basis, they can be used for rough classification of the S=O and P=O compounds in respect to catalytic vs. affinity behaviors.

The first line includes Et_2SO_4, *p*-tolyl-SO_2-OEt, *p*-tolyl-SO-OEt,

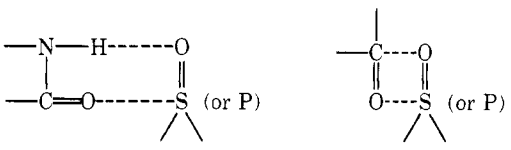
Me_2SO, and Me_2SO_2 compounds. In this series the compounds which can be absorbed more strongly in the polymer are catalytically more active in the polymerization reaction. Thus, the affinity of the compounds for both of the monomer NPCA and poly(NPCA) must be due to an essentially identical origin. Since the order in the catalytic activity is almost entirely reverse to the known order of the hydrogen bond forming property, i.e., sulfoxide > sulfone > sulfinate > sulfonate > sulfate,[11] the entity of the affinity in this series of compounds for monomer NPCA and poly(NPCA) can predominantly be caused by the contribution of positive charge on the sulfur atoms.

The second line includes non-ester-type aromatic S=O compounds, Ph_2SO and Ph_2SO_2. This line seems to cross with the first line in the neighbor of aliphatic sulfone (Me_2SO_2). The third line includes P=O compounds, $(EtO)_3P=O$, $(EtO)_2P(O)Et$, $Ph_3P=O$, and $Et_3P=O$. The slopes of the latter two lines are opposite to that of the first line, indicating that some different function must be involved.

The difference is responsible for the difference in the interactions of these two series of compounds with the monomer and poly(NPCA). The hydrogen bond forming property[10] of a variety of S=O compounds with some amides has been known to increase from sulfone to sulfoxide,[11] since the electron density on the terminal oxygen atom in the S=O compounds increases in the same order. The hydrogen bond forming property estimated for the P=O compounds from the same principle is: $Et_3P=O$ > $Ph_3P=O$ > $(EtO)_2P(O)Et$ > $(EtO)_3P=O$. Thus the predominant factor for these series of compounds in absorption to the poly(NPCA) is hydrogen bond formation between the CO–NH proton in the polymer and the terminal oxygen atoms in the S=O or P=O compound.

The diagram shown in Figure 3 clearly demonstrates that the second and the third series of compounds also interact with *monomer NPCA* through the S=O or P=O semipolar nature and behave essentially similarly to the first series of compounds in the polymerization reaction, since catalytic activities of these compounds are reverse to hydrogen bond forming properties.

Interaction of S=O or P=O Compounds with Monomer NPCA. The decrease in the catalytic activity with increasing hydrogen bonding property in all the series of compounds indicates that their interactions with the monomer NPCA, which favor the polymerization reaction, allow the following possibilities, II or III:



II III

We prefer the type II interaction for the following reasons: (i) No significant change in the chemical shift of ^{13}C-NMR spectra of the carbonyl carbon in the monomer NPCA was observed when contacted with the S=O compounds such as Et_2SO_4, Me_2SO, and Ph_2SO_2. (ii) IR spectroscopic investigation of the monomer NPCA in the presence of Ph_2SO_2 in $CHCl_3$[12] (this mixture does not polymerize during the measurement) revealed that the ν_{NH} band of the NPCA shifts to higher frequency due to dissociation of the intermolecular hydrogen bonding in the NPCA (Figure 4).

Information about the relation between polymer forming ability and dissociation of the monomer aggregation (see Appendix, section 1) was illustrated in Figure 5. Figure 5a is a plot of ν_{NH} shift caused by increasing molar ratio of Me_2SO/NPCA, and Figure 5b is that of polymer yield (in the presence of 4 mol % of Et_2SO_4 as cocatalyst) with increasing molar ratio of Me_2SO/NPCA. The maximum of the polymer yield was observed at the same molar ratio of Me_2SO/NPCA at which the dissociation of the NPCA aggregation was maximized.

Hence, we can conclude that the most important role of the S=O or P=O compound in the polymerization of NPCA is that the S=O or P=O compound dissociates the aggregated (by intermolecular hydrogen bonding) NPCA to give the solvated monomeric species ([MS]*) which is more active than its aggregated state. Since the ν_{NH} band shifts back to lower frequency by increasing the molar ratio of Me_2SO/NPCA to form a new hydrogen bond between Me_2SO and NPCA mol-

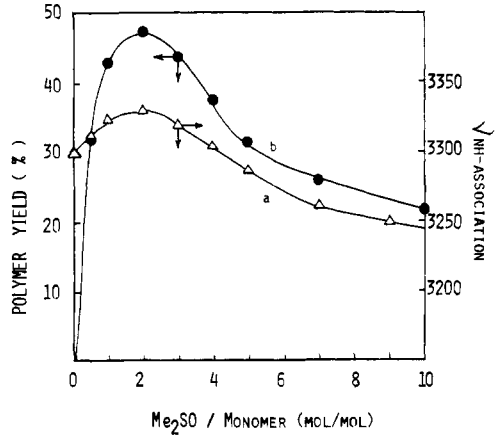


Figure 5. Parallel relation between polymerization activity of Me_2SO and variation of $\nu_{NH\ association}$ band with respect to the molar ratio of Me_2SO to NPCA monomer: (-●-) polymerization activity represented by polymer yield, (△) variation of $\nu_{NH\ associated}$ band of NPCA monomer in $CHCl_3$ solution (1.0 mol/L). Polymerization conditions: monomer, 0.0020 mol; Me_2SO–$CHCl_3$ solution, 10 mL; cocatalyst, Et_2SO_4 (4 mol % of monomer); temperature, 60 °C; time, 9 days.

ecules (see Figure 5), and since this state of the monomer becomes inert for polymerization, the most active form of the monomer must be a transient state of the two types of strongly hydrogen bonded forms. This requirement can be more properly expressed by the formulation of II (see Appendix, section 2). This interaction can also be used to explain the suppression of the ring-closing isomerization of the NPCA in the presence of the S=O or P=O compounds during the polymerization process. In addition, it interprets why nearly equimolar amounts of Et_2SO_4 and the monomer give the optimum ratio in the polymerization reaction.[2]

Another possibility that an ester-type S=O compound might form a stable salt

in a *high proportion* was excluded by NMR study. An NMR-tracing experiment for the polymerization system of NPCA containing Et_2SO_4 in $CDCl_3$ solution (Figure 6) indicated that no significant change in the ethyl proton signals of the Et_2SO_4 compound occurs throughout the polymerization. The main changes observed were upfield shifts of the ethyl and NH proton signals by ca. 4 and 5 Hz, respectively, just after mixing with the monomer. This result suggests that the solvation of Et_2SO_4 to the monomer NPCA is not accompanied by any remarkable alteration of the electronic property of the CH_2 protons in the ethyl group. This is also satisfied by the formulation of type II, and therefore type I, structure. We consider that only a small portion (probably due to a small dissociation constant of Et_2SO_4 to give Et^+ and $EtSO_4^-$ in chloroform or ethyl acetate) of the solvated monomer converts into the salt

Dissociation of the monomer

which plays a role in the initiation reaction.

The detailed polymerization mechanism seems to be considerably complicated because the polymerization process involves dissocation of the solvating molecules along with enhancement in the interaction of some of them with the polymer formed. Further, a solvated propagating (and also initiating) end would be deactivated to some extent, and the monomer addition may compete with elimination of the solvating molecule. The termination mechanism in which the degree of polymerization is restricted to ~8 is not known.

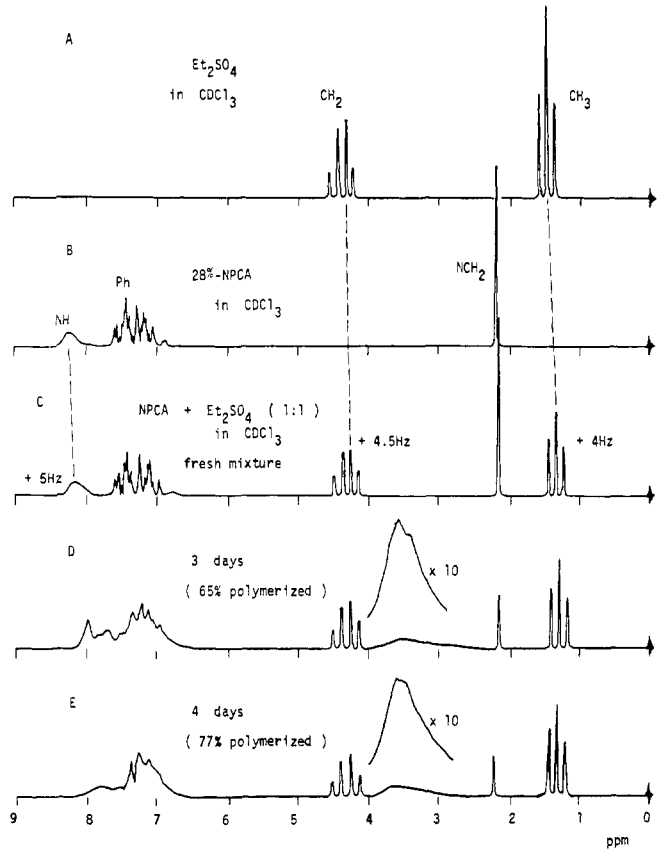
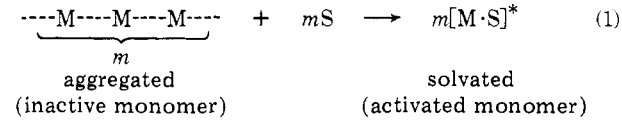


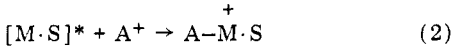
Figure 6. NMR spectra of the polymerization mixture of NPCA. A: Et_2SO_4 in $CDCl_3$ solution. B: 28% NPCA in $CDCl_3$ solution. C: Fresh mixture of A and B in an equimolar ratio of Et_2SO_4 to NPCA. D: Spectra of the mixture C after 3 days at room temperature. Conversion (65%) was determined from the relative intensity of the signals of the aziridine ring NCH_2 and of CH_3 in Et_2SO_4. E: Spectra of the mixture C after 4 days (77% polymerized). Polymerization was carried out in a sealed NMR tube. Broad polymer-NCH_2 signals are magnified (×10) and shown in the spectra D and E.

Although many uncertainties are present in this stage, the fundamental polymerization scheme can be assumed as follows:



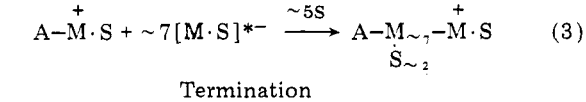
(1)

Initiation



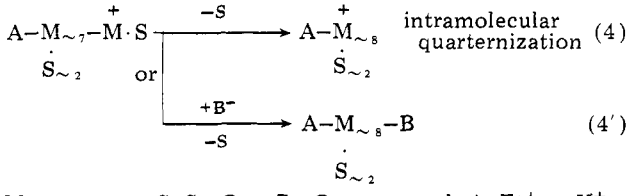
(2)

Propagation



(3)

Termination



(4)

(4′)

M, monomer; S, S=O or P=O compound; A, Et^+ or H^+; B^-, unknown (partly SO_4Et^-)

Numbers of solvating molecule are noted according to the case of Et_2SO_4.

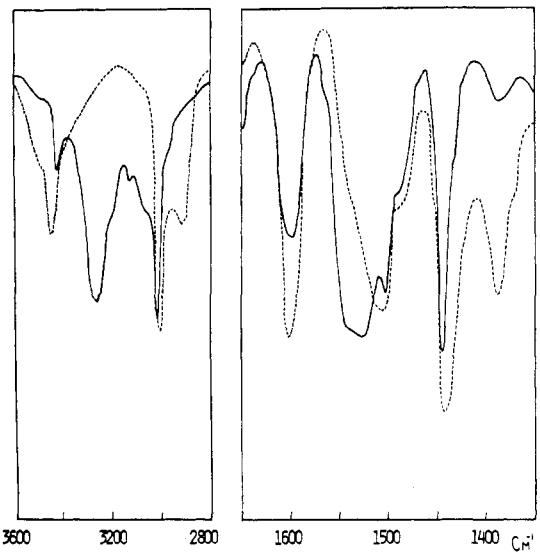


Figure 7. Concentration dependence of the IR spectra of NPCA monomer in $CHCl_3$ solution: (- - -) 0.05 mol/L, and (—) 1.0 mol/L.

Experimental Section

Materials. 1-(*N*-Phenylcarbamoyl)aziridine (NPCA) was prepared from aziridine (Nihon Shokubai Chemical Industries, Co.) and phenyl isocyanate as described in the preceding paper.[2]

Diethyl sulfate, diphenyl sulfone, tetramethylene sulfone, dimethyl sulfone, dimethyl sulfoxide, triphenyl phosphate, and triethyl phosphate were commercially available and these were used after purification.

Ethyl *p*-toluenesulfonate (*p*-tolyl-SO_2-OEt) was prepared from *p*-tolyl-SO_2Cl and ethanol.[13] Anal. Calcd from $C_9H_{12}SO_3$ (200): C, 53.97; H, 6.04; S, 16.01. Found: C, 53.70; H, 5.95; S, 15.90. *p*-Toluenesulfinate (*p*-tolyl-SO-OEt) was synthesized by the reaction of ethyl chloroformate with *p*-tolyl-SO_2Na which was prepared from *p*-tolyl-SO_2Cl with Zn/NaOH.[14] Anal. Calcd from $C_9H_{12}SO_2$ (184): C, 58.26; H, 6.57; S, 17.40. Found: C, 58.48; H, 6.61; S, 17.33. Diphenyl sulfoxide (Ph_2SO) was prepared by the reaction of benzene with $SOCl_2$.[15] Anal. Calcd from $C_{12}H_{10}SO$ (202): C, 71.26; H, 4.98; S, 15.85. Found: C, 71.34; H, 5.01; S, 16.04. Diethyl ethanephosphonate ($(EtO)_2P(O)Et$) was prepared from $P(OEt)_3$ and ethyl iodide,[16] bp 65–66 °C (3 mm); the purity was confirmed by GLC and NMR. Triphenyl phosphine oxide ($Ph_3P{=}O$) was prepared by hydroperoxidic oxidation of Ph_3P followed by thermal dehydration at 150 °C,[17] mp 157–158 °C; the purity was confirmed by NMR. Triethyl phosphine oxide ($Et_3P{=}O$) was prepared by ethylation of PCl_3 with EtMgBr, followed by hydroperoxidic oxidation,[18] bp 81–88 °C (25 mm); the purity was confirmed by GLC and NMR.

Solvents used were purified as before.[2]

Polymerization Procedure. The polymerization procedure was essentially identical with that described in the preceding paper.[2] The NPCA (0.0020 mol) and a S=O (or P=O) compound (0.0020 mol) were dissolved in dried ethyl acetate (10 mL) under argon atmosphere, then the mixture was allowed to stand at 60 °C for 23 days. When the polymer deposition was observed in the period, the polymer was separated according to the method described below. Alternatively, when no polymer was formed at the end of the period, Et_2SO_4 or other additives (4 mol % of monomer) were added and the mixture was allowed to stand at 60 °C for 23 days more.

Separation of Polymer. The polymer deposit was separated from the reaction mixture by removing the ethyl acetate solution. It was washed several times with ethyl acetate, and the insoluble fraction was dissolved in THF. After centrifugation, the polymer was reprecipitated from the THF solution by addition of ether. We denote this polymer as "washed polymer".

Removal of S=O or P=O Compound from the Polymer. Removal of the S=O or P=O compound from the "washed polymer" was performed according to the method described in the section Treatment with Amberlite-400, ii in the preceding paper.[2] The Amberlite-treated polymer contains S or P atom at almost the same level of analytical accuracy in the measurements used. We denote this polymer as "freed polymer".

Reabsorption of S=O or P=O Compound to the Polymer. Equimolar amounts (0.0020 mol) (one monomer unit in the polymer was regarded as 1 mol) of a S=O or P=O compound and the finely pulverized "freed polymer" were mixed in ethyl acetate and the suspension in a sealed tube was allowed to stand at 60 or 3.5 °C for 8 days. Then the polymer was recovered by the method described in the section Separation of Polymer.

Apparatus. IR spectra were recorded with Hitachi-EPI-2 and Nihon-Bunko Model DS-402 spectrometers. NMR spectra were recorded with Varian A60D and T-60 apparatus. Gel permeation chromatography was employed to examine the molecular weight and its distribution of the polymers prepared, by means of a Shimadzu-Du Pont Model 803 apparatus with column constitution of SG-60-40-20 and eluted with THF at 45 °C.

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Appendix

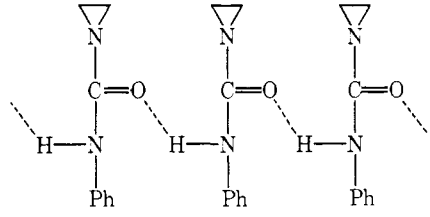
(1) IR Study of Aggregation of 1-(*N*-Phenylcarbamoyl)aziridine. Concentration dependences of the IR ν_{NH} and amide II bands of 1-(*N*-phenylcarbamoyl)aziridine in $CHCl_3$ (Figure 7) provide a feature of the aggregation state of this compound.

ν_{NH}: The 1 mol/L solution showed two bands at 3270 cm^{-1}(broad) and 3430 cm^{-1} (sharp). Since the dilute solution (0.05 mol/L) showed no broad band at 3270 cm^{-1}, this band can be assigned to $\nu_{NH\ associated}$, and therefore the 3430 cm^{-1} band can be assigned to $\nu_{NH\ free}$.

Amide II bands: Relative absorbance of the 1540 cm^{-1} band (*trans*-amide) to the 1440 cm^{-1} band (*cis*-amide) in the two concentrations revealed that trans amide is predominant in the 1 mol/L solution and cis amide is predominant in the 0.05 mol/L solution.

δ_{NH}: The 1 mol/L solution showed stronger absorption at 1550 cm^{-1} ($\delta_{NH\ associated}$) than the case of the 0.05 mol/L solution. The reverse is true for the 1530 cm^{-1} ($\delta_{NH\ free}$) band.

On the basis of these IR studies, it can be concluded that NPCA exists as aggregated state through intermolecular hydrogen bonding under such a concentration as used in the polymerization reaction (0.2 mol/L).



(2) Indication of Cis Configuration of the Amide Group in NPCA in the Presence of Diphenyl Sulfone. Figure 4 shows the IR spectra of 1.0 mol/L solutions of NPCA in $CHCl_3$ in the presence and absence of an equimolar amount of diphenyl sulfone. The relative absorbance of the 1440 cm^{-1} band (*cis*-amide) to the 1540 cm^{-1} band (trans amide) is higher in the presence of diphenyl sulfone compared with the NPCA compound alone. Although diphenyl sulfone is a weaker solvating reagent than diethyl sulfate and the system seems to be a ternary mixture of solvated NPCA, free NPCA, and free sulfone, it may be possible to suggest that the solvated NPCA molecule has a type II structure involving a *cis*-CO-NH configuration.

References and Notes

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Macrocyclic Formals. 3. Two-Stage Polymerization of 1,3-Dioxacycloalkanes

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ABSTRACT: 1,3-Dioxacycloalkanes were found to polymerize in two stages forming cyclic oligomers in the first stage and mainly high polymers in the second stage with boron trifluoride ether complex as an initiator. Some of the formed cyclic oligomers were isolated and identified. High-speed liquid chromatography was used to obtain product distribution and preparative chromatography was also used.

There have been extensive works on the polymerization of 1,3-dioxolane. Mainly four kinds of reaction mechanism have been proposed, namely, carboxonium ion,[1] tertiary oxonium ion,[2] macrocyclic secondary oxonium ion,[3] and polymer complexed tertiary oxonium ion[4] mechanisms. There are some evidences for each mechanism but they are not always consistent to each other. We have been interested in the polymerization of cyclic formals.[1a,5-7] We proposed the carboxonium ion mechanism. Recently, we and Black and Worsfold independently reported the two-stage polymerization of 1,3-dioxacycloalkanes.[8-10] We reported that 1,3,6,9-tetraoxacycloundecane is polymerized in two stages initiated with boron trifluoride ether complex forming cyclic oligomers in the first stage and high polymers in the second stage. Black and Worsfold reported that 1,3-dioxolane is polymerized by two different mechanisms operating at the same time giving low molecular weight material and high polymers with triethyloxonium hexafluorophosphate as an initiator. Although the reaction conditions employed are different, the results seem to be very similar in the sense of two-stage character of monomer consumption. In the two-stage polymerization of 1,3-dioxacycloalkanes, the products can be separated by liquid chromatography and the information on reaction mechanism can be derived by studying the structure and amount of the products. In order to establish the two-stage character of the polymerization of 1,3-dioxacycloalkanes, the polymerizations of 1,3-dioxolane, 1,3-dioxacyclooctane, 1,3,6-trioxacyclooctane, 1,3,6,9,12-pentaoxacyclotetradecane, and 1,3,6,9,12,15-hexaoxacycloheptadecane were studied using boron trifluoride ether complex as an initiator. The polymerizations were found to proceed in two stages in all cases. The results on 1,3-dioxolane are very important, which may reflect the true reaction mechanism of the polymerization of 1,3-dioxolane.

Experimental Section

Dichloromethane and boron trifluoride ether complex were distilled under nitrogen. 1,3-Dioxacyclooctane, 1,3,6-trioxacyclooctane, 1,3,6,9,12-pentaoxacyclotetradecane, and 1,3,6,9,12,15-hexaoxacycloheptadecane were synthesized from the corresponding glycols and paraformaldehyde using *p*-toluenesulfonic acid as catalyst by a method similar to one in the literature.[11] They were dried and purified by distillation over lithium aluminum hydride four times. 1,3-Dioxolane was distilled over calcium hydride followed by distillation over lithium aluminum hydride. The purity of the dioxacycloalkanes was shown to be better than 99.9% by gas chromatography. The reaction was carried out by adding boron trifluoride ether complex to a dichloromethane solution of 1,3-dioxacycloalkane in a one-necked flask fitted with a three-way stopcock capped with a serum cap. The reaction was stopped by adding an excess amount of triethylamine. The consumption of monomer was monitored by gas chromatography on the sample pulled out from the system with a syringe through the serum cap. The gas chromatograph used in the experiment is Hitachi Model K53 connected with 1 m of column packed with Silicone GE SE-30 and FID detector was used. The product distribution was recorded on Toyo Soda high-speed liquid chromatograph Model HLC 802 UR connected with 2 m of TSK-GEL G2000 H8 (exclusion limit 2.5×10^2 Å, TP/F 8000) columns and 1 m of TSK-GEL G4000 H8 (exclusion limit 1×10^4 Å, TP/F 8000) column (Toyo Soda) unless otherwise noted. The detector for gel chromatography is a differential refractometer. The solvent is chloroform and the flow rate is 1 mL/min at 35 °C. Three counts approximately correspond to 2 mL of elution volume. The higher count number indicates the lower molecular weight.

Results

Typical examples of the time–conversion relationship of 1,3-dioxacycloalkanes initiated with boron trifluoride ether complex in dichloromethane, obtained by plotting the disappearance of monomer against time, are shown in Figure 1. Together with the results on gel chromatography which are shown in Figures 2–5, the monomer seems to be consumed in two stages forming cyclic oligomers in the first stage and high polymers in the second stage. For instance, the consumption of 1,3,6,9,12-pentaoxacyclotetradecane seems to be one stage in Figure 1 because the reaction is fast; however, in the earlier stage only cyclic oligomers are formed and mainly high polymers are formed in the latter stage of the polymerization as is reported.[12] The gel chromatogram indicates that oligomers are formed during the first relatively slow stage and high