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Synthesis and Electronic Effect of the Substituents on Anionic Ring-Opening Polymerization of Para-Substituted Phenyl Cyclopropanes

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Abstract : As an extension of studies in the anionic polymerization of activated cyclopropanes with electronically push-pull substituents, p-substituted phenylcyclopropane-l,l-dicarbonitriles having MeO, Me, H, Cl, and NO_2 as substituents were prepared. The electronic effects of substituents upon the ring-opening reaction during anionic polymerizations were examined by determining the rate constants of polymerizations, conversions and molecular weights of the resulting polymers. The rate constants of polymerization(k_P) in DMSO by 2 mole% cyanide ion at 35 ℃ were p-MeO=0.45, p-Me=0.14, p-H=0.07, p-Cl=0.06 and p-NO_2=0.011liter/mole.sec, and the rate constants of polymerization in DMSO by 5 mole% pyridine at 35 ℃ were p-Me0=0.048, p-Cl=7.6 x 10^{-3} and p-NO_2=1.64 x 10^{-3}liter /mole.sec., respectively. The electronic effect exerted by substituents were well consistent with the Hammett relationship(log $k/k_o = \sigma \rho$) when Brown's σ^+ constants were used. The reaction sensitivity constants(ρ) obtained from cyanide ion initiator were -1.0 and -0.94 for pyridine initiation. These results indicate that the anionic ring-opening polymerization of p-substituted phenylcyclopropanes is carried out via highly conjugated zwitterionic transition state in the ring opening reaction. Furthermore, in the case of the polymerization initiated by pyridine or triethylamine, the formation of macrozwitterion during polymerization is a feasible mechanism.

INTRODUCTION

Cyclopropane compounds have aroused many controversial problems such as ring strain, ring structures, transmission of resonance effects, classical or nonclassical nature of cyclocarbinyl species, etc. Cyclopropane compounds have been found to undergo ring-opening by addition reactions with electrophilic, nucleophilic and radical species[1-3] Ring-opening by addition reactions may be the most characteristic features of cyclopropane chemistry, and it shows a marked resemblance to carbon-carbon double bonds, From the results of thermodynamic data of polymerization of some small ring compounds, ring-opening polymerization of those compounds appears possible. In the case of cyclopropane itself, some evidence of polymerization has been reported. However the conversion and the molecular weight were low.[4-8] Also, many cyclic compounds have

enough thermodynamic driving force for polymerization. However, they failed to polymerize unless they overcome high energy of activation in the ring-opening process. We have worked on the syntheses and ring-opening polymerization of various cyclic monomers such as 1,1-disubstituted-2-vinylcyclopropanes,[9-13] 1,1-disubstituted phenylcyclopropane,[14] 2-phenyl-3-vinyloxirane,[15] 1-(p-substituted phenyl)-2-vinyl cyclopropanes,[16] spiro(vinylcyclopropanes),[17] 10-methylene-9,10-dihydroanthryl-9-spirocyclo-propanes,[18] substituted 3,4-dihydro-2H-pyrans,[19] substituted 2-methylene-1,3-dioxolanes,[20,21] dihydrofurans,[22] α-vinyl cyclic sulfones,[23,24] vinylketene cyclic acetal,[25] In these monomer-to-polymer systems, proper methods were adopted to bond activation and stabilization of propagating reactive sites.

Successful instances in which cyclopropanes were polymerized anionically were 1,1-disubstituted 2-vinylcyclopropanes[13] and phenylcyclopropane-1,1-dicarbonitrile[14] such as 2-vinylcyclopropane-1,1-dicarbonitrile and ethyl 1-cyano-2-vinylcyclo propanecarboxylate polymerized cleanly in 1,5-fashion by radical initiators,[9,10] however in anionic polymerization only ring-opening took place without participation of vinyl groups and also ring-opening took place in the same manner with phenylcyclopropane. This interesting polymerization behavior of substituted cyclopropanes has been attributed to their unique electronic properties, that is, activation of a bond by the formation of push-pull system[26-29] with proper positioning of negative- and positive-charge distributing substituents. Another contributing factor is the proper stabilization of a formed anion by the attack of nucleophile.

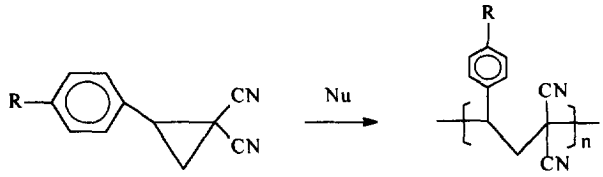
In order to explore the electronic effect of push-pull substituent system during anionic ring-opening polymerization, para-substituted phenylcyclopropane-1,1-dicarbonitriles were prepared, and the electronic effects of substituents in ring-opening reaction were interpreted by examining the polymerization behaviors, the conversions, and the molecular weights of resulting polymers.

RESULTS AND DISCUSSION

Synthesis of Substituted Phenylcyclopropanes. p-Substituted phenylcyclopropane-1,1-dicarbonitriles were prepared from the photo-initiated radical chain reaction of bromomalononitriles with styrenes or from thermally initiated radical chain reaction of bromomalononitrile with p-nitrostyrene, followed by the dehydrobromination with triethylamine for ring closure. p-Substituted phenylcyclopropane-1,1-dicarbonitriles such as 2-phenylcyclopropane-1,1-dicarbonitrile(PCP-DCN), p-methylphenylcyclopropane-1,1-dicarbonitrile (Me-PCP-DCN), p-methoxyphenylcyclopropane-1,1-dicarbonitrile(MeO-PCP-DCN), p-chlorophenyl cyclopropane-1,1-dicarbonitrile(Cl-PCP-DCN) and p-nitrophenylcyclopropane-1,1-dicarbonitrile(NO_2-PCP-DCN) were prepared according to the above procedure. However, the reaction with p-nitrostyrene was carried out via thermal reaction due to no photo reaction.

Polymerizations. p-Substituted phenylcyclopropane-1,1-dicarbonitriles were subjected to polymerization. by ionic or nonionic nucleophiles. The results of ring-opening polymerizations were summarized in Table 1 and 2. The typical behavior of anionic polymerization in aprotic media where termination is not expected, were observed in the present system. When an additional feed of monomer was introduced to the completed polymerization mixture, the successive polymerization took place and the molecular weights varied as the amount of initiator. Notable exceptions to this concept were poly NO_2-PCP-DCN and poly MeO-PCP-DCN. Though the conversion of the polymerization of these monomers were almost 100%, the molecular weights

were lower than those of others and didn't show dependence to the amount of initiator. In the case of NO_2-PCP-DCN, the increased acidity of the p-nitrobenzylic proton of the polymer backbone or monomers may cause easy chain transfer to polymer chains or monomers.



R= H-, Me-, MeO-, Cl-, NO_2-

Scheme 1. Nucleophilic ring-opening polymerization of cyclopropane monomers.

Table 1. Ring-Opening Polymerization under Various Conditions

R	Run No.	Solvent	Nucleophile (mole %)	Temp. (℃)	Time (hr)	Conv. (%)	η_{inh} (dL/g)	Decomposition.[a] (℃)
H	1	DMSO	3.3(NaCN)	24	16	95	0.227	330
	2	DMSO	1.1(NaCN)	25	10	80	0.324	
	3	DMSO	0.33(NaCN)	25	24	25	0.337	
	4	DMF	1.5(NaCN)	15	24	100	0.354	
	5	DMF	0.5(NaCN)	10	16	100	1.00	
	6	DMF	0.3(NaCN)	15	24	90	1.327	
	7	DMF	1.0(Py)	25	36	90	0.572	
Me	1	DMSO	3.3(NaCN)	24	16	100	0.198	330
	2	DMSO	1.1(NaCN)	25	10	100	0.404	
	3	DMSO	0.33(NaCN)	25	24	35	0.41	
	4	DMF	1.5(NaCN)	15	24	100	0.259	
	5	DMF	0.5(NaCN)	10	16	80	0.506	
	6	DMF	1.0(Py)	25	36	50	0.31	
MeO	1	DMSO	3.3(NaCN)	24	16	100	0.089	312
	2	DMSO	1.1(NaCN)	25	10	100	0.136	
	3	DMSO	0.33(NaCN)	25	24	100	0.143	
	4	DMF	1.5(NaCN)	15	24	100	0.090	
	5	DMF	0.55(NaCN)	10	16	100	0.14	
	6	DMF	0.15(NaCN)	16	24	100	0.156	
	7	DMF	1.0(Py)	25	36	100	0.136	
Cl	1	DMSO	3.3(NaCN)	24	16	100	0.116	300
	2	DMSO	1.1(NaCN)	25	10	100	0.25	
	3	DMSO	0.33(NaCN)	25	24	100	0.76	
	4	DMF	1.5(NaCN)	15	24	100	0.13	
	5	DMF	0.5(NaCN)	10	16	100	0.36	
	6	DMF	0.15(NaCN)	15	36	100	0.82	
	7	DMF	1.0(Py)	25	36	100	0.78	
NO_2	1	DMF	1.5(NaCN)	15	24	100	0.103	292
	2	DMF	0.5(NaCN)	10	24	100	0.13	

[a] Initial decomposition temperature was measured by DSC with a heating rate of 5 °C/min.

T_g and T_m were not observed.

In view of deep violet color occurrence, during the reaction between sodium cyanide and NO_2-PCP-DCN, the mechanism of reaction seemed to involve the development of highly conjugated carbanion resulted from the proton abstraction at the nitrobenzylic position by cyanide ion. Since the absorption in the visible region (at

540nm and 1090nm) by this species persisted throughout the polymerization, the same mechanism could be operative also in the propagation step. The similar phenomena were observed in the anionic polymerization of meta- and para-nitrostyrenes.[30] On the other hand, it is not clear why the polymerization of MeO-PCP-DCN involving no visible absorption during polymerization give lower molecular weights.

Table 2. Ring-Opening Polymerization in Nucleophilic Solvents

Monomer (100mg)	Solvent (ml)	Temp. (℃)	Time (day)	η_{inh} (dL/g)
H-PCP-DCN	Py(1)	15	1	0.22
	Py(0.2) + CH_2Cl_2(1)	15	6	0.334
	TEA(0.2) + CH_2Cl_2(1)	15	4	0.424
Me-PCP-DCN	Py(1)	15	1	0.18
	Py(0.2) + CH_2Cl_2(1)	15	3	0.231
	TEA(0.2) + CH_2Cl_2(1)	15	2	0.34
MeO-PCP-DCN	Py(l)	15	1	0.090
	Py(0.2) + CH_2Cl_2(1)	15	1	0.130
	TEA(0.2) + CH_2Cl_2(1)	15	1	0.156
Cl-PCP-DCN	Py(1)	15	1	0.096
	Py(0.2) + CH_2Cl_2(1)	15	7	0.151
	TEA(0.2) + CH_2Cl_2(1)	15	5	0.348
NO_2-PCP-DCN	Py(l)	15	1	0.085

In the kinetics of ring-opening polymerization, the rate of polymerization by cyanide ion was about 10 times faster than that by pyridine. The difference in the polymerization rate is probably attributable to the nature of counter ions, and the considerable amount of precipitation occurred in pyridine-initiated polymerization which may implies the formation of macrozwitter ion aggregates. In several anionic and cationic polymerizations initiated by uncharged Lewis bases and by uncharged Lewis acids, the formation of zwitterions in the initiation process has been postulated, and macrozwitterions formations in the polymerization of lactones[31,32] and sultones[33] initiated by tertiary amines were successful.

From the fact that the polymerization performed in pyridine solution or triethylamine solution gives considerably high molecular weights, the rate of initiation is much slower than that of propagation. Charge separation is generally energetically unfavorable and with the less nucleophilic amines even small amounts of enthalpy, lost in this way, may markedly reduce the initiation rate.

Determining of the Propagation Rate Constants. Kinetics of the polymerization has been studied by using ^1H NMR spectroscopy. Kinetics of the ring-opening polymerization by cyanide ion and pyridine initiator are shown in figure 1. The rate constant was obtained from the slope of the straight line in the plot of ln{[Mlo/[M]} against time, The results are summarized in Table 3

Hammett Relationship. By plotting the relative reactivity expressed in logarithmic form of k_{MeO}/k_H, k_{Me}/k_H, k_H/k_H, k_{Cl}/k_H and k_{NO2}/k_H against Brown's σ^+ values. The reaction constants determined from the slope of the straight lines in figure 1 have values of ρ = -1.0 and -0.94 for cyanide ion and pyridine initiators, respectively.

Mechanism Study. Hammett equation has been applied to a limited extent in mechanistic polymer chemistry. The treatment has been used to study the free radical polymerization of styrene,[34] cationic

polymerization of styrenes[35,36] and vinyl phenyl ethers,[37] Ziegler-Natta polymerization of styrenes,[38] anionic polymerization of 4-nitrostyrenes,[30] and reaction of polystyryl anions with styrene.[39]

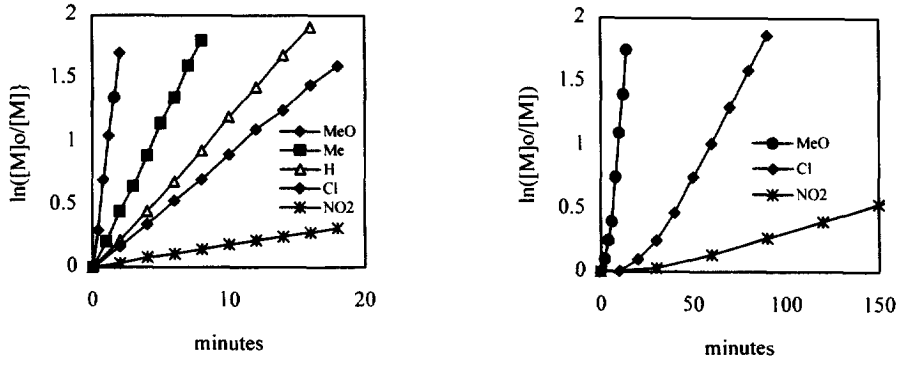


Fig. 1. Plots of kinetics in the ring-opening polymerization of cyclopropanes initiated by 2 mole% CN^- ion (left) and by 5 mole% pyridine(right) in DMSO solvent at 35 ℃.

Table 3. Kinetic Data of Ring-Opening Polymerization of P-Substituted 2-Phenylcyclopropane -1,1-dicarbonitriles in DMSO-d_6 Solvent at 35 ℃

Monomer	Substituent constant		by CN^- (2 mole%)			by Pyridine-d_5 (5 mole%)		
	σ_p	σ_p^+	k_p (l/mole sec)	(k_p/k_o)	$\log(k_p/k_o)$	k_p (l/mole sec)	(k_p/k_o)	$\log(k_p/k_o)$
P-MeO	-0.27	-0.78	0.45	6.43	0.81	0.048	6.3	0.80
P-Me	-0.17	-0.31	0.144	2.06	0.31	-	(2.5)*	(0.4)*
P-H	0	0	0.070	1	0	-	(1.2)*	(0.09)*
P-Cl	0.23	0.11	0.065	0.930	-0.032	0.0076	1	0
P-NO_2	0.78	0.79	0.011	0.157	-0.80	0.0016	0.22	-0.67
				ρ = -1.0			ρ = -0.94	

* Comparison with p-Cl at 5 % conversion

It is apparent that a knowledge of whether a given reaction follows the Hammett σ or σ^+ constants should be a diagnostic assistance in the study of reaction mechanism. Those reactions which follow the σ^+ constant must involve an electronically deficient intermediate of some type in the transition state, whereas the reaction which follows the σ values must proceed without the formation of such an intermediate. By plotting $\log k_p/k_o$ against Brown's σ^+ values,[40] where k_p is the second-order propagation rate constant of p-substituted PCP-DCN derivatives, a straight line was obtained. These results indicate that the polymerization of these monomers involved the development of conjugated positive charge in the rate determining step.

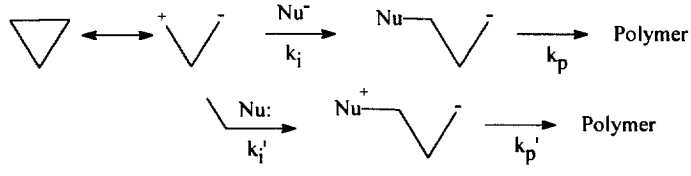
Generally, in the ring-opening polymerization, propagation occurred via S_N2 pathway. Concerning with rate dependence on the electronic effect of substituents, sometimes electron-withdrawing substituents accelerate and sometimes decelerate S_N2 reactions. In fact, steric effects are avoidable with meta- and para-substituted benzylic compounds[41-44]. However, substituents influence the S_N2 reactions of such substrates in a very complex

manner[43], all the para-substituted benzyl chlorides, regardless of the substituent being electron-donating or -withdrawing, react faster than the unsubstituted compound with thiosulfate. As is well known, in the activated complex of S_N2 reaction, bond making and bond breaking have not necessarily occurred to the same extent. If the entering group is very nucleophilic and donates electron more than the leaving group is withdrawing them, then the positive charge on the carbon should decrease, and the rate is increased by electron-withdrawing groups; but if X is an excellent leaving group and withdraws electrons more than Y supplies them, then the partial positive charge on the reacting carbon should increase the rate and electron-withdrawing substituents should decrease the rate.[41] Of course, if the situation described becomes very pronounced, the mechanism will be changed to S_N1.

One formulation of the intermediate-mechanism theory is that of Sneen.[45,46] The formulation is in fact very broad and applies not only to borderline behavior but to all nucleophilic substitution at a saturated carbon.[47,48] According to Sneen, all S_N1 and S_N2 reactions can be accommodated by one basic mechanism(the ion-pair mechanism). The substrate first ionizes to an intermediate ion pair which then proceeds to products.

$$RX \underset{}{\overset{k_1}{\rightleftharpoons}} R^+X^- \overset{k_2}{\rightleftharpoons} \text{Product}$$

The difference between the S_N1 and S_N2 mechanism is that in the former case the formation of ion pair(k_1) is rate-determining, while in the S_N2 mechanism its destruction (k_2) is rate-determining. Borderline behavior is found where the rate of formation and destruction of the ion pair are of the same order of magnitude. Other evidence for ion-pair mechanism comes from a linear free-energy relationship which was discovered to hold between the stability of a carbenium ion and its selectivity,[49,50] but this relationship holds only where free carbenium ions are present.[51] Linear free-energy relationships have also been used to support the conception that the ion-pair mechanism operates not only on secondary but also on primary substrates,[52-55] which have traditionally been regarded as showing pure S_N2 behavior.[56-59]



where for CN^- $k_i = k_1$, $k_i \geq k_p$; Pyridine $k_i' < k_p'$ and $k_p > k_p'$

Scheme 2. Ring-opening mechanism of activated cyclopropane.

In our monomer systems, Brown's σ^+ value of Hammett relationship which hold for the anionic polymerization means that ion pair is placed on in the reaction coordinate. The similar trends of Hammett plots under different nucleophilicities of initiators means ring-opening polymerizations of activated cyclopropanes undergo similar transition states of rate determining step even though extents of polymerization rates are quite different. On the basis of the above concepts, the mechanism of the anionic ring-opening polymerization of p-substituted PCP-DCN compounds could be depicted as scheme 2.

The structural features of carbanion-carbenium ion pairs as intermediates in anionic ring-opening polymerization are envisioned as favoring such a transformation are as follows:

(1) The covalent bond to be cleaved should be highly activated by charge distribution substituents and by ring strain to become vulnerable for cleavage.

(2) Carbanion-stabilizing substituents should be attached to one of the carbon atoms and carbenium ion-stabilizing substituents to the other carbon atom for constituting the C-C bond cleavage by the attack of nucleophile on the carbenium character position.

The additional evidences of carbanion-carbenium ion pairs as discrete intermediates shown by Cram et al.[26-29,60] in the racemizations and solvolyses of the substituted cyclopropanes with electron-donating and -withdrawing groups are also consistent with the above explanations.

EXPERIMENTAL

Preparation of para-Substituted Styrenes. Styrene, p-methylstyrene, p-methoxystyrene, and p-chlorostyrene were available from Tokyo Kasei Chemical Co.(Japan). P-Nitrostyrene was prepared by the reaction of decarboxylation of p-nitrocinnamic acid. Decarboxylation was carried out by the method for the decarboxylation of formylcinnamic acid 61. 25g(0.13mole) of p-nitrocinnamic acid was dissolved in 150ml of quinoline and 0.1g of copper acetate was added. The solution was added dropwise to 3g of copper powder in a 50ml distilling flask heated to 300 ℃. The addition was regulated such that there was no appreciable quantity of liquid in the distilling flask whenever. The distillate was poured into 500ml of 3N HCl solution. The mixture solution was extracted with three 100ml portions of dichloromethane. The dichloromethane extracts were washed with dilute HCl solution, and then with water. After drying over anhydrous magnesium sulfate, the dichloromethane was evaporated. The residue was distilled under reduced pressure(1mmHg, 67 ℃) to give 12g of p-nitrostyrene as a yellow liquid, recrystallized as thick needles from petroleum ether, m.p. 21 ℃.

2-Phenylcyclopropane-1,1-dicarbonitrile(PCP-DCN).[62,63] Bromomalononitrile(14.5g, 0.1mole) and 11.4g (0.11mole) of styrene were dissolved in 100 ml of dichloromethane. The solution was introduced into a Pyrex tube and then irradiated with a UV light in a Rayonet Photochemical Reactor with three RPR 350nm lamps at a distance of 15cm. Irradiation was performed under a nitrogen atmosphere at room temperature for 3hr. Upon the completion of the irradiation, the reaction mixture was diluted with an additional 100ml of dichloromethane and was subjected to dehydrobromination by the dropwise addition of 11.1g(0.11mole) of triethylamine at 0 ℃ for 30 min. The precipitated triethylamine hydrobromide was separated by filtration and filtered solution was washed with dilute hydrochloric acid and again with distilled water, After the solution was concentrated on a rotary evaporator, the crude product was recrystallized from a mixture of methanol and n-hexane(50:50 by volume) and finally sublimed at 75 ℃(ca. 0.1mmHg) to give 13.4 g (80% yield) of PCP-DCN, m.p. 60 ℃.

p-Methylphenylcyclopropane-1,1-dicarbonitrile(Me-PCP-DCN). Me-PCP-DCN was prepared by the similar procedures for PCP-DCN. The crude product was purified by recrystallization from methanol and sublimed at 80 ℃ to afford 85% yield, m.p. 77 ℃.

p-Chlorophenylcyclopropane-1,1-dicarbonitrile(Cl-PCP-DCN). Cl-PCP-DCN was prepared from the

same manner to that described in the PCP-DCN preparation. The product was recrystallized from methanol and sublimed at 130 ℃, 80% yield, m.p.126.5 ℃.

p-Methoxyphenylcyclopropane-l,l-dicarbonitrile (MeO-PCP-DCN). The preparation of MeO-PCP-DCN was similar to that of PCP-DCN. But using a less polar solvent such as benzene rather than dichloromethane gave better results under low temperature condition(below 0 ℃) during the UV irradiation, so a jacketed reaction tube was employed for cold reaction. Dehydrobromination was also performed below 0 ℃. The crude product was recrystallized from methanol followed by sublimation at 85 ℃, 85% yield, m.p. 78.5 ℃.

p-Nitrophenylcyclopropane-1,1-dicarbonitrile (NO_2-PCP-DCN). Photolytic reaction was not effective for the reaction of p-nitrostyrene with bromomalononitrile, and the following procedure was employed. A solution of 15g(0.1mole) of p-nitrostyrene and 14.5g(0.1mole) of bromomalononitrile in 100ml of chloroform was refluxed for a period of 20hr until no double bond would be exhibited by NMR spectra of reaction mixture. The reaction mixture was then treated with 11.1g(0.11mole) of triethylamine at 0 ℃ to perform dehydrobromination. The mixture was washed with dilute HCl and water, followed by purification by column chromatography on silica gel, 200-mesh(elution with CH_2Cl_2-hexane; 2 to 1 by vol.), and upon the removal of solvent was obtained a brown semisolid. Sublimation(at 130 ℃, 0.1mmHg)from the crude solid gave 4 g (18.6% yield) of NO_2-PCP-DCN, m.p. 129.5 ℃.

Ring-Opening Polymerization of Cyclopropanes. The monomers were dissolved in dry DMF or in other solvents to produce 0.5-1 M solution. Then a calculated amount of a standard solution of initiator (NaCN saturated in DMF at 25 ℃; 0,15N, NaCN saturated in DMSO; 0.33 N, pyridine in DMF or other solvents) was added at proper temperature. Distinct color developed immediately, when pyridine was used as an initiator. NO_2-PCP-DCN exhibited deep violet color In the basic solution. During the polymerization, no precipitation occurred except the case of Me-PCP-DCN in DMF. However the polymer of PCP-DCN obtained from the reprecipitation in methanol was not soluble in DMF. The polymerizations under these conditions gave high conversion yields. Inherent viscosity values were determined in DMF or in conc. sulfuric acid. The monomer was also subjected to polymerization in nucleophilic solvent systems such as pyridine or 1:5 mixture of triethylamine and dichloromethane. The polymers obtained under these conditions were also high molecular weight polymers, and bulk polymerizations performed above the m.p. of monomers with one drop of triethylamine were completed within a few minutes to give light yellow transparent rigid solids. Attempts to initiate polymerization of the monomers with radical or cationic initiators were unsuccessful.

Representative Polymerization of PCP-DCN by Nucleophiles. The following polymerization procedure of PCP-DCN exemplifies the polymerization procedures employed for the various monomers studied. Monomer PCP-DCN (1 m mole) was placed in a glass ampoule and to it was added 1ml of dry DMF. The ampoule was stoppered with a rubber septum cap, and then chilled in a dry ice-acetone bath. To this solution was added 0.1 ml of initiator solution (NaCN saturated in DMF; 0.15N) by a microsyringe. The ampoule was evacuated and sealed. The sealed ampoule was maintained at proper temperature. Upon the completion of polymerization the ampoule was opened and the solution was poured into a 15 ml of methanol. The precipitated polymer was

washed thoroughly with methanol, and then dried under vacuum at 40 ℃ for 24 hr. The conversion was quantitative. The product polymer was found insoluble in common solvents but soluble in conc. sulfuric acid. Inherent viscosity values were determined in conc. sulfuric acid.

Kinetics of Ring-Opening polymerization. The reaction rates of various nucleophiles with a monomer were determined by NMR method. The reaction was monitored by measuring the integration values of disappearing proton peaks. A typical procedure, described here for the case of PCP-DCN is as follows.

Monomer PCP-DCN (0.42m mole, 70mg) was placed in an NMR tube. To it was added 0.25 ml of dry DMSO-d_6. The NMR tube was then stoppered with a rubber septum cap under N_2 purge. At first, the integration of the peaks by protons positioned at 2 and 3 carbon atoms (chemical shifts; 3.3, 2.2 ppm) of PCP-DCN under the condition of no initiator was considered as the value at t=0. Using a 50 μ l microsyringe, 29 μ l of initiator solution (NaCN saturated in DMSO-d_6; 0.33N) was injected at time t=0, giving an initiator concentration of 2.3 mole %. The resulting solution was quickly shaken, and the progress of polymerization was followed by observing the steady decrease in ^{1}H-NMR integration value. Readings were taken at 1 minute intervals. Integration values were converted to conversions, and plotted against time. The slope of the line gives the observed rate of polymerization R_p, expressed in mole/liter.sec. The rate constant k_p was then calculated using the expression $R_p = - d[M]/dT = k_p[M][M^-]$, $\ln\{ [M]_o/[M] \} = k_p [M^-]t$, where $[M^-]$ was assumed to be equal to the initiator concentration.

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