Effect of High Pressure on Radical Polymerizability of Acryl- and Methacrylamides Capable of Forming Stable Radicals

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ABSTRACT: Some acryl- and methacrylamides capable of forming stable radicals were prepared from acryloyl or methacryloyl chlorides with *N*-(4-aminophenyl)benzeneamine and *N*-(4-aminophenyl)-4-methoxybenzeneamine. Radical polymerization of these monomers was studied in tetrahydrofuran at 60 °C under pressure up to 15 kbar with the use of 2,2′-azoisobutyronitrile (AIBN), dibenzoyl peroxide (DBP), cumene hydroperoxide (CHP), and tetraethylthiuram disulfide (TETD) as initiators. Under pressure below 13 kbar, TETD produced no polymer, while the use of DBP and CHP resulted in a normal polymerization at pressures higher than 4 kbar. Polymerization occurred normally under any pressure only when AIBN was used as the initiator. The change of activation volume of polymerization, ΔV^*, of *N*-(4-anilinophenyl)acrylamide in the presence of AIBN becomes larger with increasing pressure (pressure and ΔV^* are given in kbar and cm^3/mol): 0, −36; 1, −31; 2, −22; 3, −15; 4, −10; 5, −6.4. The intrinsic viscosities of the polymers were found in tetrahydrofuran at 30 °C to be 0.16 to 0.17 and to be independent of the nature of the monomer or of the pressure.

Some acryl- and methacrylamides bearing a hindered arylamine group capable of forming stable radicals are prepared,[1] and the radical polymerization of one of those amides, *N*-(4-anilinophenyl)acrylamide, has been studied[2] with various radical initiators under atmospheric pressure. The polymerization goes normally only when 2,2′-azoisobutyronitrile is used, whereas other initiators such as dibenzoyl peroxide, cumene hydroperoxide, and tetraethylthiuram disulfide inhibit the polymerization completely.

The kinetic changes caused by pressure, on the other hand, have often been reported[3] to alter the rate and direction of chemical reactions. Thus, we tried to investigate the initiating ability of these initiators on the polymerizability of such acryl- and methacrylamides under high pressures up to 15 kbar. A preliminary part of the high pressure research has already been communicated[4] and the present paper gives details of the reaction.

Experimental Section

Reagents. The monomers, acryl- and methacrylamides of *N*-(4-aminophenyl)benzeneamine and *N*-(4-aminophenyl)-4-methoxybenzeneamine, were prepared from acryloyl and methacryloyl chlorides with a corresponding arylamine by the method of Braun and Hauge[1] and recrystallized from hexane. The properties of the monomers are given in Table I.

All of the initiators were commercially available products and purified in the standard manner before use: 2,2′-Azoisobutyronitrile was twice recrystallized from a methanol solution and dried on phosphorus pentoxide in vacuo. Dibenzoyl peroxide was twice precipitated from a chloroform solution with methanol and dried by evacuation. Cumene hydroperoxide was purified via its sodium salt by the procedure of Walling and Chang,[5] and tetraethylthiuram disulfide was recrystallized from a benzene solution with petroleum ether and dried at reduced pressure.

Reagent grade tetrahydrofuran was distilled from a mixture of activated alumina and sodium hydroxide pellet into a receiver containing sodium chips, distilled in an atmosphere of dry nitrogen, and finally vacuum-distilled from lithium aluminum hydride before use. Dioxane and hexane were both reagent grade and purified by refluxing over sodium wire for several hours and distilling through a 30-cm column from sodium. Middle fractions were collected for use. Methanol was reagent grade and used after fractional distillation.

Polymerization Procedure. Experiments at atmospheric and high pressures were carried out in a high-pressure reactor designed by us[6] and manufactured by Kobe Steel, Ltd., described in detail previously.[6,7]

A monomer was dissolved in 16 mL of dry tetrahydrofuran followed by the addition of some amounts of an initiator. The solution was then transferred to a polymerization vessel which was degassed and sealed under a stream of nitrogen free from oxygen. The vessel was placed in a reactor at 60.0 ± 0.5 °C for convenient intervals under atmospheric or high pressure up to 15 kbar. Application of pressure produced a small temperature rise in the system due to adiabatic compression, but measurements of pressure and temperature changes on the system containing only the pressure-transmitting fluid (a mixture of methanol and glycerine) indicated that equilibrium was restored within 5 to 10 min. A few minutes were also required to open and close the reactor. After the reaction, pressure was relieved via the release valve, the closure opened, and the sample removed. The reaction mixture was then dissolved into a small amount of tetrahydrofuran and poured into anhydrous petroleum ether to remove the unreacted monomer and the initiator. The insoluble material was collected and washed with cooled methanol. A blue or brownish solid was purified by redissolving twice and reprecipitating in a large excess of nonsolvent. It was finally dried to constant weight under vacuum at room temperature.

High-Pressure Apparatus. The high-pressure apparatus which was employed is essentially a device for placing reaction mixtures under hydrostatic pressures up to 15 kbar. It consists basically of a low-pressure unit, a pressure intensifier, a reactor vessel, pressure gauge, and auxiliary equipment, manufactured by Kobe Steel, Ltd., Kobe. The components were described in detail previously.[6] In operation, an internal reaction vessel containing the system under study is placed in the reactor vessel which is filled with pressure-transmitting fluid and the reactor closure put in place. A pressure of approximately 1 kbar is applied directly by the low-pressure pump and then increased to the desired pressure via the intensifier. The pressure on the low-pressure side of the intensifier is next released, and the system becomes isolated by the closing of check valves. During a run the temperature of the reactor vessel is kept as constant as ±0.5 °C by the band heater. It takes normally about 5 min for the system to reach the required temperature and pressure. Because of this and because of the few minutes required to open and close the reactor, rate measurements are only feasible on reactions with half-lives of an hour or more. When a reaction is completed, pressure is relieved via the intensifier and the release valve, the closure opened, and the internal reaction vessel removed. The necessity of isolating reaction systems from the hydraulic fluid in our apparatus requires some sort of internal reaction vessel which is chemically inert and which can change its capacity without damage. Several devices have been employed for this purpose, but for the work described here, a simple piston-cylinder type vessel made of stainless steel has been used, as shown previously.[7]

Test Methods. The IR absorption spectra in the region of 400 to 4000 cm^{-1} were measured for the samples by a Hitachi Model EPI-G3 infrared spectrophotometer. The samples were prepared by the KBr pellet technique.

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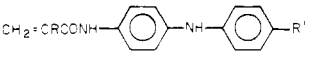
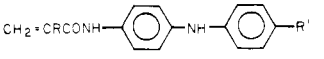
Table I
N-Substituted Acryl- and Methacrylamides[a]



R	R′	yield, %	mp,[b] °C	C, % calcd	C, % found	H, % calcd	H, % found	N, % calcd	N, % found
H	H	63	152-153	75.60	75.73	5.92	5.99	11.76	11.54
H	CH_3O	58	109-110	71.62	71.47	6.01	6.18	10.44	10.12
CH_3	H	53	104-105	76.16	76.15	6.39	6.25	11.10	10.82
CH_3	CH_3O	46	116-117	72.32	72.13	6.43	6.19	9.92	10.14

[a] Prepared by the method of Braun and Hauge[1] and recrystallized from hexane. [b] Uncorrected values.

Table II
Effects of Pressure and Initiators on the Polymerization of N-Substituted Acryl- and Methacrylamides[a]



R	R′	pressure, kbar	AIBN yield, %	AIBN $[\eta]$,[b] dL/g	DBP yield, %	DBP $[\eta]$,[b] dL/g	CHP yield, %	CHP $[\eta]$,[b] dL/g	TETD yield, %	TETD $[\eta]$,[b] dL/g
H[c]	H[c]	0	3.78		0.0		0.0		0.0	
		4	35.6	0.162	20.8	0.163	39.2	0.163	0.0	
		10	44.2	0.165	42.2		43.2	0.165	0.0 (14.8)[d]	(0.163)[d]
		15	47.2	0.166	46.8	0.165	45.8	0.164	29.4	0.165
H	CH_3O	0	8.31		0.0		0.0		0.0	
		4	40.4	0.165	26.7	0.163	41.0	0.165	0.0	
		10	54.6		53.3		54.2		0.0 (16.9)[d]	
		15	56.7	0.163	56.1	0.165	54.7	0.162	34.7	0.164
CH_3	H	0	14.5		0.0		0.0		0.0	
		4	52.0		29.6	0.170	46.2	0.168	0.0	
		10	71.8	0.167	63.2		63.1		0.0 (19.2)[d]	
		15	74.0	0.170	64.2	0.169	66.2	0.171	41.6	0.169
CH_3	CH_3O	0	19.2		0.0		0.0		0.0	
		4	58.1	0.171	32.6		50.1		0.0	
		10	76.7		68.7	0.168	69.8	0.167	0.0 (24.5)[d]	
		15	78.9	0.169	70.2	0.171	68.9	0.170	47.8	0.172

[a] 0.262 mol/L of a monomer were polymerized with 1.86×10^{-3} mol/L of an initiator in tetrahydrofuran at 60 °C for 24 h. AIBN, 2,2′-azoisobutyronitrile; DBP, dibenzoyl peroxide; CHP, cumene hydroperoxide; TETD, tetraethylthiuram disulfide. [b] In tetrahydrofuran at 30 °C. [c] Data of Tanaka et al. in ref 4. [d] Value for a polymer obtained at 13 kbar.

The intrinsic viscosities of the polymers were obtained in tetrahydrofuran with a Ubbelohde type viscometer at 30.00 ± 0.02 °C. The points were taken by succesive dilutions of the original concentration.

Results and Discussion

Blue or brownish polymers were obtained by radical polymerization of the acryl- and methacrylamides of *N*-(4-aminophenyl)benzeneamine and *N*-(4-aminophenyl)-4-methoxybenzeneamine in tetrahydrofuran under high pressure up to 15 kbar with the use of various initiators such as 2,2′-azoisobutyronitrile, dibenzoyl peroxide, cumene hydroperoxide, and tetraethylthiuram disulfide at 60 °C for 24 h. The concentrations of the monomers and an initiator were 2.62×10^{-1} and 1.86×10^{-3} mol/L, respectively, and the results are shown in Table II. Under pressure higher than 4 kbar, the polymerizations of these monomers occurred normally by using these initiators except tetraethylthiuram disulfide which inhibited the polymerization completely until the pressure reached 13 kbar. The polymerization rates increased monotonously with pressure and reached an equilibrium value at a certain pressure independent on the nature of the initiator except of tetraethylthiuram disulfide. The initiators like 2,2′-azoisobutyronitrile and cumene hydroperoxide were found to be much more effective and to have larger rates of polymerization than dibenzoyl peroxide, and the latter was more effective than tetraethylthiuram disulfide.

In Figure 1, the rate, R_p, of polymerization of *N*-(4-anilinophenyl)acrylamide is correlated with pressure; the units of R_p being mole per liter per sec. Although the

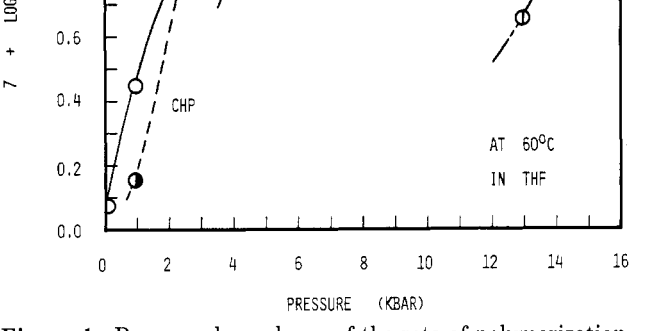


Figure 1. Pressure dependence of the rate of polymerization, R_p, of *N*-(4-anilinophenyl)acrylamide in tetrahydrofuran at 60 °C with various initiators: ○, 2,2′-azoisobutyronitrile; ⊖, dibenzoyl peroxide; ◑, cumene hydroperoxide; ⊕, tetraethylthiuram disulfide.

points indicate some curvature in a log R_p–pressure plot in the range of pressure up to 15 kbar, they give an overall value of the activation volume, ΔV^*: eq 1 of Van't Hoff[8] or Evans and Polanyi[9] relates reaction rate constants to pressure,

$$\mathrm{d} \ln k/\mathrm{d}P = -\Delta V^*/RT \qquad (1)$$

Table III
Effect of Time on Polymerization of N-(4-Anilinophenyl)acrylamide with AIBN and DBP[a]

time, h	AIBN yield, %	AIBN [η],[b] dL/g	DBP yield, %	DBP [η],[b] dL/g
5	6.93		7.20	
8	22.9	0.161	16.4	0.160
16	35.1		33.6	0.161
24	45.5	0.164	41.9	0.163
32	54.7	0.164	53.2	0.164

[a] 0.262 mol/L of the monomer were polymerized with an initiator (1.86×10^{-3} mol/L) in tetrahydrofuran at 60 °C under 7 kbar. AIBN, 2,2′-azoisobutyronitrile; DBP, dibenzoyl peroxide. [b] In tetrahydrofuran at 30 °C.

where k is the specific rate constant, R the gas constant, T the absolute temperature, and P the pressure. The activation volume is the volume change in going from the ground state to the transition state. If the reaction path, on the other hand, remains the same under pressure, the polymerization of these monomers at high pressure obeys eq 2,

$$R_p = -d[M]/dt = k_p(k_d f/k_t)^{1/2}[I]^m[M]^n \quad (2)$$

where [M] and [I] indicate the concentrations of an initiator and a monomer; k_d, k_p, and k_t are the rate constants for initiator decomposition, chain propagation, and chain termination, respectively, and $m = 1$ or $^1/_2$. The initiating efficiency, f, of an initiator may vary with pressure. From eq 1 and 2, and assuming $k = k_p(k_d f/k_t)^{1/2}$, we can obtain ΔV^* with a log R_p–pressure plot.

Such a curvature in a plot as that in Figure 1 might be anticipated since a small transition state could well be less compressible than the larger reactants so that the activation volume becomes a function of pressure. This may indicate a somewhat larger negative value of ΔV^* near atmospheric pressure and the data of R_p, indeed, extrapolate to uncertain but large negative values of ΔV^* at zero pressure (ΔV^* and pressure are given in cm³/mol and kbar): with 2,2′-azoisobutyronitrile, −36, 0; −31, 1; −22, 2; −15, 3; −10, 4; −6.4, 5. The mean experimental value in the range 0 to 1 kbar, calculated from the acceleration of the polymerization at 1 kbar, is −36 cm³/mol. As mentioned later, the order, n, of reaction with respect to the concentration of the monomer was found to be 2.4 which was used in these calculations. No activation volume has been reported for this monomer, but the experimentally determined values can be compared with those[10] for various monomers (monomer and ΔV^* are given): styrene, −16 to −18; methyl methacrylate, −17 to −26; allyl acetate, −13; vinyl acetate, −9; acenaphthylene, −6 cm³/mol. Overall values of ΔV^* for the other monomers used here seem to be similar to that of N-(4-anilinophenyl)acrylamide, judging from the data in Table II.

If the rate of polymerization is described by eq 2, the apparent rate constant is composed of k_d, k_p, and k_t. Accordingly, ΔV^* is also made up of three terms,

$$\Delta V^* = \Delta V_p^* + (\Delta V_d^* - \Delta V_t^*)/2 \quad (3)$$

where ΔV_d^*, ΔV_p^*, and ΔV_t^* are the volume changes associated with initiator decomposition, chain growth, and chain termination, respectively. The volumes of activation for the dissociation of 2,2′-azoisobutyronitrile, dibenzoyl peroxide, and *tert*-butyl peroxide are obtained as 3.8 or 9.4 cm³/mol at 70 or 62.5 °C, 4.8 to 9.7 cm³/mol at 60 to 80 °C, and 5.4 to 13.3 cm³/mol at 120 °C, severally, in various solvents such as toluene, carbon tetrachloride, cyclohexene, and benzene at 1 atm (1.01325 bar).[10] The measurements of k_t at high pressure could not permit an accurate evaluation of ΔV_t^*, but for styrene or methyl methacrylate it appears to be about two or three times as large as ΔV_d^* (monomer and ΔV_t^* in cm³/mol are given[11]): styrene, 13; vinyl acetate, 16; butyl methacrylate, 18; butyl acrylate, 21; methyl methacrylate, 25.

From eq 3, using $\Delta V_d^* = +4$ with 2,2′-azoisobutyronitrile and +9 with dibenzoyl peroxide, and $\Delta V_t^* = +13$ or 20 cm³/mol, ΔV_p^* can be calculated to be about −28 or −32 cm³/mol with 2,2′-azoisobutyronitrile, and −30 or −34 cm³/mol with dibenzoyl peroxide, respectively. The values for various monomers are found[11] to be as (monomer and ΔV_p^* in cm³/mol are given): styrene, −12 to −18; methyl methacrylate, −19; butyl acrylate, −23; butyl methacrylate, −23; vinyl acetate, −24. The comparison may be satisfactory in view of the approximations involved, but more precise determinations of the values of the activation volumes, ΔV_p^* and ΔV_t^*, are desirable.

The time dependence of the polymerization was investigated with a 2.62×10^{-1} mol/L solution of N-(4-anilinophenyl)acrylamide and the result was shown in Table III. The polymerization was carried out in tetrahydrofuran at 60 °C with use of a solution (1.86×10^{-3} mol/L) of 2,2′-azoisobutyronitrile or dibenzoyl peroxide as the initiator. The rate of polymerization increased monotonously with time and reached a maximum or an equilibrium value at a certain reaction time both under atmospheric pressure[2] and under a pressure of 7 kbar.

Table IV shows the effect of the initiator concentration on the rate of polymerization of N-(4-anilinophenyl)-acrylamide. The polymerization of the monomer (2.62×10^{-1} mol/L) was carried out in tetrahydrofuran at 60 °C for 24 h with 2,2′-azoisobutyronitrile under the pressure of 1 kbar and with dibenzoyl peroxide at 4 kbar. In Figure 2, the logarithm of the rate of polymerization is plotted against the logarithmic value of the concentration, [I], of the initiator. The best straight line was found by the least-squares method and, from the slope, the order of reaction with respect to the concentration of 2,2′-azo-

Table IV
Effect of Initiator Concentration on Polymerization of N-(4-Anilinophenyl)acrylamide[a]

initiator concn, 10^{-3} mol/L	with AIBN at 1 kbar: polymer yield, g	polymer yield, %	R_p, 10^{-7} mol/L/s	[η],[b] dL/g	with DBP at 4 kbar: polymer yield, g	polymer yield, %	R_p, 10^{-7} mol/L/s	[η],[b] dL/g
1.86	0.092	9.22	2.80	0.160	0.206	20.8	6.26	0.163
9.36	0.256	25.7	7.78	0.162	0.378	37.9	11.5	
13.0					0.405	40.6	12.3	0.160
18.6	0.322	32.3	9.79	0.161	0.415	41.6	12.6	
27.9	0.338	33.9	10.3	0.159	0.546	54.7	16.6	0.156
37.2	0.377	37.8	11.5	0.157				

[a] The monomer (0.262 mol/L) was polymerized in tetrahydrofuran at 60 °C with AIBN (2,2′-azoisobutyronitrile) at 1 kbar or with DBP (dibenzoyl peroxide) at 4 kbar for 24 h. R_p, the rate of polymerization. [b] In tetrahydrofuran at 30 °C.

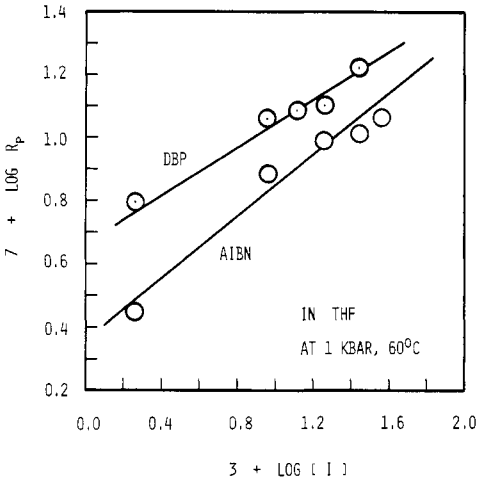


Figure 2. Effect of concentration, [I], of an initiator, dibenzoyl peroxide (⊙) or 2,2′-azoisobutyronitrile (○), on the rate of polymerization, R_p, of *N*-(4-anilinophenyl)acrylamide (0.262 mol/L) in tetrahydrofuran at 60 °C under 1 kbar.

Table V
Effect of Concentration of *N*-(4-Anilinophenyl)acrylamide on Polymerization with 2,2′-Azoisobutyronitrile at 1 kbar[a]

monomer		polymer yield		R_p, 10^{-7} mol/L/s
g	mol/L	g	%	
0.499	0.131	0.040	8.02	1.22
0.697	0.183	0.061	8.75	1.85
0.998	0.262	0.092[b]	9.22	2.80
1.496	0.393	0.457	30.5	13.9
1.995	0.524	0.658	33.0	20.0

[a] The monomer was polymerized in tetrahydrofuran at 60 °C for 24 h in the presence of 1.86×10^{-3} mol/L solution of the initiator. R_p is the rate of polymerization. [b] The intrinsic viscosity, [η], of the material in tetrahydrofuran at 30 °C is 0.160.

isobutyronitrile or dibenzoyl peroxide is obtained as 0.51 or 0.38. The exponent of the initiator concentration remains approximately equal to 0.5, which shows that the kinetic chains are still terminated in pairs under these conditions.

The variations of the rate of polymerization at various initial concentrations (0.131 to 0.524 mol/L) of *N*-(4-anilinophenyl)acrylamide were investigated, where a 1.86×10^{-3} mol/L solution of 2,2′-azoisobutyronitrile was used as the initiator and tetrahydrofuran was used as the solvent. Table V shows the result obtained at 60 °C for 24 h under pressure of 1 kbar. In Figure 3, logarithm of the rate of polymerization, R_p, is plotted against the logarithmic value of the concentration, [M], of the monomer. The fit of the points to the straight line is by no means good, but the best straight line was obtained by the least-squares method. From the slope, the order of reaction, *n*, with respect to the concentration of the monomer is found to be 2.4. To account for this higher exponent of the monomer concentration, a more detailed study of the initiating reaction should be desirable.

Small amounts of the samples of poly[*N*-(4-anilinophenyl)acrylamide] and poly[*N*-(4-anilinophenyl)methacrylamide], obtained with tetraethylthiuram disulfide at 15 Kbar, were decomposed with sodium by Lassaigne's method[12,13] and identified by the methods of Shriner, Fuson, and Curtin[12] and of Feigl:[13] A solution obtained by decomposition of the polymeric material, which was produced with tetraethylthiuram disulfide, was acidified with acetic acid. To this a few drops of lead acetate solution were added and a black precipitate of lead sulfide

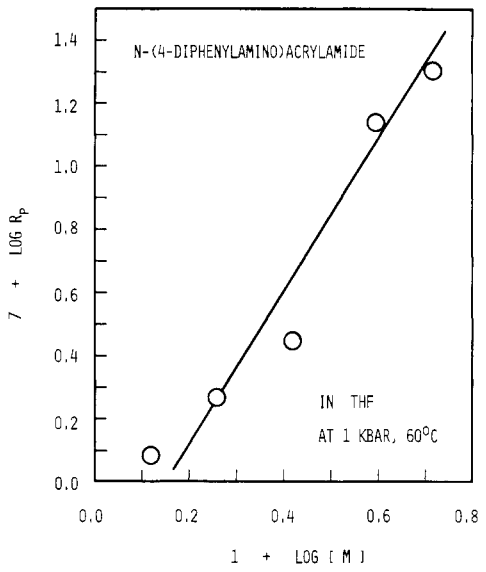


Figure 3. Effect of the monomer concentration, [M], on the rate of polymerization, R_p, of *N*-(4-anilinophenyl)acrylamide in tetrahydrofuran with 2,2′-azoisobutyronitrile (1.86×10^{-3} mol/L) at 60 °C under 1 kbar.

was found to form; this indicates sulfur. Thus, these polymeric materials seem to contain some fragments of the initiator.

Aliphatic nitriles are characterized[14] by weak to medium absorption at the region of 2260–2240 cm^{-1} in the infrared spectrum. No sharp but weak and broad absorption bands were observable at the corresponding frequencies in the spectra of the polymers obtained. The differential infrared spectroscopy, which is useful for the identification or quantitative estimation of minor constituents in organic substances,[15-17] was applied to but failed in the detection of the nitrile end groups in the polymeric materials. There was no significant difference in the carbon–nitrogen triple-bond stretching region among the infrared spectra of the polymers obtained with 2,2′-azoisobutyronitrile and those of the materials with the other initiators.

The polymers obtained with these initiators had characteristic bands due to the N–H stretching, the N–H bending, and the C=O stretching vibrations of secondary amides[14] in 3400–3060, 1600–1515, and near 1660-cm^{-1} regions, respectively. The interaction bands between the N–H bending and the C–N stretching of the C–N–H group[14] were found near 1250 cm^{-1}. The absorption bands assigned to the N–H stretching, the N–H bending, and the C–N stretching vibrations of secondary amino groups[14] were also observed in the regions of 3400–3310 cm^{-1}, near 1515 and 1350–1300 cm^{-1}, severally, of the spectra of these samples. The characteristic band at 940 cm^{-1} due to the out-of-plane hydrogen deformation mode[14] of olefinic C–H groups was observed in the spectra of the monomers but disappeared in those of the polymers. The bands at 1660–1640 cm^{-1} assigned to the stretching vibration of the carbon–carbon double bond of olefinic hydrocarbons[14] were obscured by overlapping of the C=O stretching and the N–H bending bands.

The molecular weights of the polymers were not determined, but intrinsic viscosities in tetrahydrofuran were measured at 30 °C, and these give an approximate indication of the pressure effect as shown in Table II. The intrinsic viscosities seem neither to vary with pressure nor to depend on the nature of the initiator. The acceleration of the polymerization can be ascribed to an increase in the rate of chain propagation and a decrease in the rate of termination of kinetic chains. If there were no other effects

the molecular weight of the polymer would rise with pressure instead of no variation. The bimolecular transfer reaction between polymer radicals and monomer molecules is probably accelerated nearly as much by pressure as the chain growth reaction. In this transfer reaction the growing molecular chain is terminated, but a new radical is formed to continue the kinetic chain. Moreover, in the polymerization of these monomers the chain transfer reaction should be sufficiently large to account for the termination of most of the molecular chains, although the kinetic chains still end by the coupling or disproportionation of pairs of long-chain radicals. The intrinsic viscosities of poly[*N*-(4-anilinophenyl)acrylamide] obtained using different concentrations of 2,2′-azoisobutyronitrile have been found to vary only slightly with polymerization rate as shown in Table IV. This suggests there is much transfer in the polymerization. No variation in the molecular weight may represent the achievement of an unaltered balance between the rates of chain growth and chain transfer in the range of pressure up to 15 kbar.

In the reaction of oxy and carbon radicals with *N*-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)-*tert*-butylamine *N*-oxide,[18] the former radicals are found to abstract the phenolic hydrogen of the compound to produce a stable radical, whereas the latter add preferentially to the α carbon of the nitrone to yield a stable nitroxide radical. The results of this polymerization can be elucidated in the light of the above observation: Under atmospheric pressure, the radicals formed by decompositions of dibenzoyl peroxide, cumene hydroperoxide, and tetraethylthiuram disulfide may abstract mainly hydrogen of the amino group of the monomer to inhibit polymerization, while the carbon radicals resulting from 2,2′-azoisobutyronitrile add preferentially to the vinyl double bonds to initiate polymerization, as shown by eq 4. Such a

$$CH_2{=}CRCONHC_6H_4NHC_6H_4R' \xrightarrow{R''O\cdot,\ R''S\cdot} CH_2{=}CRCONHC_6H_4\dot{N}C_6H_4R' \quad (4a)$$

inhibition

$$CH_2{=}CRCONHC_6H_4NHC_6H_4R' \xrightarrow{R''\cdot} R''CH_2\dot{C}RCONHC_6H_4NHC_6H_4R' \quad (4b)$$

polymerization

selectivity of these radicals, however, would diminish or disappear with increasing pressure. The radicals from dibenzoyl peroxide and cumene hydroperoxide, and also the thio radicals from tetraethylthiuram disulfide, therefore, tend to add to the vinyl double bonds of this monomer to initiate polymerization under high pressure, although their additivity to the monomers may be very sensitive to increase in pressure and their initiating efficiencies are different from each others.

As shown in Table II, the methacrylates and the monomers containing a methoxy group polymerize faster, which might be due to the electronic natures or the polar effects of the methyl and the methoxy groups of these monomers. The relative reactivity of the monomers, such as the Alfrey-Price Q and e values,[19,20] has not yet been reported nor determined in this experiment, but can be estimated with the values of various acrylamides and methacrylamides, $CH_2{=}CRCONHR'$ (R, R′, Q, and e are given[19]): H, H, 1.18 or 1.120,[20] 1.30 or 1.190;[20] H, C_8H_{17}, 0.19, −0.02; H, *t*-C_8H_{17}, 0.20, −0.10; H, $C_{18}H_{37}$, 0.660,[20] 1.130;[20] H, CH_2OH, 0.390,[20] 0.610;[20] CH_3, H, 1.46, 1.24; CH_3, CH_3, 0.320, −0.600; CH_3, C_2H_5, 0.70 or 0.250,[20] −0.88; CH_3, C_6H_5, 0.85, −0.78; CH_3, $C_6H_4CH_3$, 1.20, −0.76; CH_3, C_6H_4Cl, 0.70, −0.98; CH_3, $C_6H_4OCH_3$, 2.80, −1.19; CH_3, $CH_2C_6H_5$, 1.140,[20] 1.710.[20]

The Q and e values of various alkyl acrylates and methacrylates are found[21,22] to be correlated with the polarity of their substituents, such as the Taft's σ^* values[23] which are the substituent constants dependent only upon the net polar effect of the substituents relative to methyl group. The Q values, as well as the e values, of some kinds of nucleo-substituted phenyl methacrylates are also correlated[21] with the Hammett's σ constants,[23] and described[21] by a more significant contribution of the resonance effect than that of the inductive nature of the substituents. A similar situation should be encountered in our case: The reactivity differences in polymerization of the acrylamides and the methacrylamides may be explained by the polar effect ($\sigma^* = -0.100$, $\sigma' = -0.05$ for CH_3; $\sigma^* = \sigma' = 0.00$ for H), and those between the monomers with and without the methoxy group should be elucidated with the resonance effect ($\sigma_p = -0.27$, $\sigma_p - \sigma' = -0.50$ for CH_3O; $\sigma_p = \sigma_p - \sigma' = 0.00$ for H) rather than the inductive effect ($\sigma' = -0.23$ for CH_3O) of the methoxy group of the monomers.

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