Radical Bulk Polymerization of N-Vinylcaprolactam

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Synopsis

Bulk radical polymerization of N-vinylcaprolactam was studied at temperatures between 60 and 120°C. with different initiators. Satisfactory results were obtained with azobisisobutyronitrile, *tert*-butyl perbenzoate, and *tert*-butyl peroxide as initiators. The polymerization reaction of N-vinylcaprolactam with these initiators is first order with respect to the monomer and 0.5 order with respect to the initiator. A linearity of the kinetic curves up to high conversions was observed. The cause of this behavior is a feeble gel effect, which also induces an increase of the molecular weight during polymerization.

N-vinylcaprolactam polymerization was studied with H_2O_2 and benzoyl peroxide as initiators at temperatures over 100°C.; low molecular weight polymers were obtained.[1,2] Satisfactory results were obtained with azobisisobutyronitrile as initiator,[3] but there are no published data on the kinetics of this reaction.

Experimental

The monomer was obtained by vinylation of caprolactam with acetylene in the presence of caprolactyl potassium.[1,4] N-Vinylcaprolactam was isolated from the reaction mass by distillation at reduced pressure (8–10 mm.) under argon; it then was purified by being distilled twice under argon at 8–10 mm. through a rectification column (ϕ = 30 mm., h = 700 mm.) filled with glass rings (ϕ = 4 mm., h = 5 mm.), the reflux ratio being 80%; the fraction was collected directly in ampules at temperatures between 110.8 and 111.2°C. The ampules containing pure monomer were closed under argon. In such conditions pure N-vinylcaprolactam (n_D^{40} = 1.5057, freezing point 34.5°C.) may be conserved a long time at room temperature in the dark.

The pure monomer was handled only under dry, inert atmosphere.

The precautionary measures of purifying, conserving, and handling of the N-vinylcaprolactam were necessary because of the sensitivity of this monomer to the action of oxygen, which oxidizes rapidly to a brown-yellow compound. The presence of such compounds diminishes considerably the activity of N-vinylcaprolactam in the polymerization reaction, and the results of kinetic measurements became unreproducible.

The polymerization was accomplished in closed ampules and in dilatometers with mercury. The ampules and dilatometers, after being filled with monomer and initiator, were conditioned by three cycles of freezing at −50°C., air-removal at 10^{-2} mm., filling with purified argon, and warming at 370°C. Finally the ampules were closed and put in a thermostat at the polymerization temperature, maintained within ±0.05°C. We observed a satisfactory agreement between the results obtained by gravimetric and dilatometric methods (except for the polymerization of N-vinylcaprolactam in the presence of large amounts of $tert$-butyl perbenzoate).

Some polymerizations were carried out in open ampules, in order to establish the influence of atmospheric oxygen on the reaction.

In the case of the polymerization in ampules as well as in the case of some dilatometric experiments the polymer yield was determined gravimetrically; the reaction mass was dissolved in carbon tetrachloride, and the polymer was precipitated in petroleum ether and dried at 70–80°C. at 60 mm.

The polymers of N-vinylcaprolactam were characterized by their intrinsic viscosities, determined in toluene at 25°C. and calculated from the following formula:[5]

$$[\eta] = [2(\eta_{sp} - 2.303 \log \eta_r)]^{1/2}/c$$

The following initiators were used: azobisisobutyronitrile (AIBN), from Fluka A.G., Buchs S.G., benzoyl peroxide recrystallized from chloroform, lauroyl peroxide, $tert$-butyl peroxide (PTB), $tert$-butyl perbenzoate (PBTB), from Elektrochemische Werke-München, cyclohexanone hydroperoxide (50% with dibutyl phthalate), and cumene hydroperoxide.

RESULTS and DISCUSSION

In Tables I and II are presented some results of the bulk polymerization of N-vinylcaprolactam with different initiators in air.

TABLE I

		Polymer yield, %			
Initiator	C_i, %	6 hr. at 60°C.	7.5 hr. at 80°C.	7.5 hr. at 100°C.	5 hr. at 117°C.
Cumene hydroperoxide	2.2–2.3	0	9	75	85
Trigonox A 75	1.6–1.7	0	0	73	—
$tert$-Butyl peroxide	2.0–2.2	0	0	94	—
$tert$-Butyl perbenzoate	1.8–2.0	71	—	95	—
lauroyl peroxide	0.8–1.0	—	7	5	3
Cyclohexanone hydro-peroxide	2–3	0	7	10	—
Benzoyl peroxide	2	0	0	0	—
AIBN	0.1	27	—	—	—

TABLE II

Initiator	C_i, %	Temp., °C.	Time, hr.	Yield, %
tert-Butyl perbenzoate	1.8–2.0	80	1.5	65
Cyclohexanone hydro- peroxide	4.8	117	5	20
AIBN	0.1	80	2	76

The data show that AIBN is an active initiator of N-vinylcaprolactam radical bulk polymerization; used in relatively low concentrations, it produces high conversions in the temperature range from 60 to 80°C. At the same temperatures PBTB is fairly active. At higher temperatures (80–100°C.) Trigonox A 75, PTB, and cumene hydroperoxide are active. The peroxides of the organic acids (benzoyl and lauroyl peroxides) are not efficient initiators. In the case of benzoyl peroxide no polymerization was observed, even in the absence of air. The behavior of this type of peroxide probably is due to a secondary reaction (redox) with the monomer, taking place at a higher rate than the polymerization, so that the initiator is con-
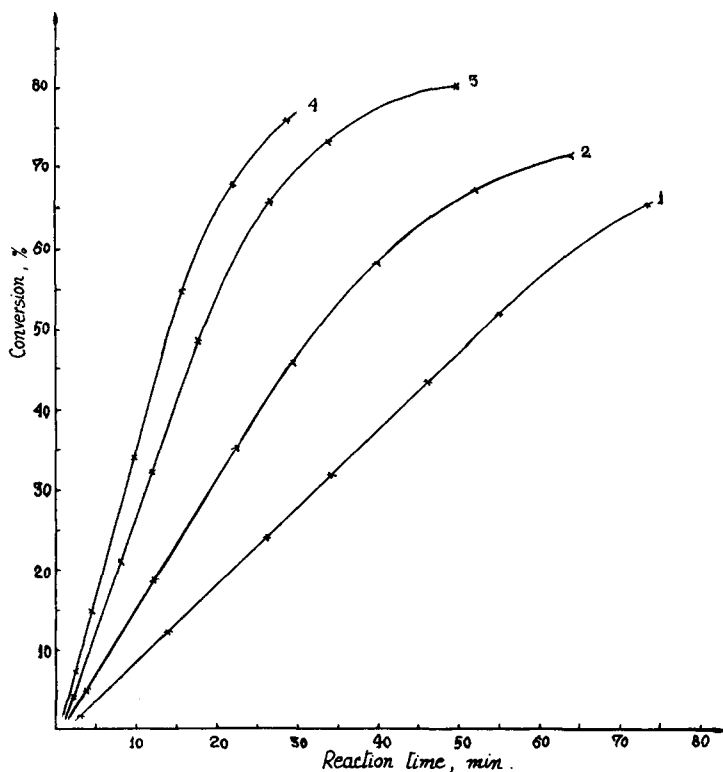

Fig. 1. Dilatometric curves of N-vinylcaprolactam bulk polymerization at 75°C. with different AIBN concentrations (%): (1) 0.1; (2) 0.15; (3) 0.2; (4) 0.25.

sumed, and one can observe a brown-yellow color of the reaction mass. Such a color was not observed in the case of the other initiators in the absence of air.

In Figure 1 are presented the kinetic curves of N-vinylcaprolactam polymerization at different AIBN concentrations and constant temperature, and in Figure 2 are shown the results of polymerizations at different temperatures and constant AIBN concentration. One can see that relatively low AIBN concentrations (0.1–0.25% by weight initiator in monomer)
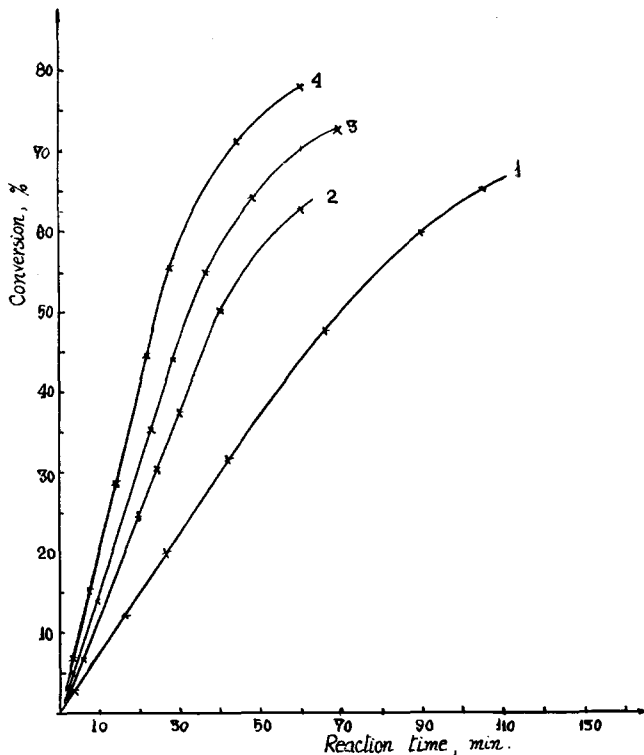

Fig. 2. N-vinylcaprolactam bulk polymerization with 0.15% AIBN: (1, 3, 4) determined dilatometrically at 70, 75, and 80°C.; (2) determined gravimetrically in the presence of air at 75°C.

permits the achievement of high conversions (70–80%) in a relatively short time (0.5–2.5 hr.). The limit of conversion increases with the temperature at which the polymerization occurs.

By comparing curves 2 and 3 of Figure 2 one observes that atmospheric oxygen diminishes the rate of N-vinylcaprolactam radical bulk polymerization. That effect was verified in the case of other initiators, too. Atmospheric oxygen influences the reaction, not only by diminishing its rate, but also by diminishing the molecular weight of the polymer, as one can see from the data presented in Table III.

TABLE III

Initiator C_i, %	Temp., °C.	Convsn.,[a] %	$[\eta]$, dl./g. (toluene, 25°C.)	Atmos.[b]
AIBN				
0.15	75	72	0.86	I
0.15	75	50	0.60	A
0.15	75	68	0.68	A
0.15	80	77	0.70	I
0.25	75	75	0.74	I
PBTB				
0.5	75	36	0.26	I
1.5	75	66	0.21	I
1.5	85	80	0.15	I
21.5	65	—	0.07	I
21.4	75	74	0.05[c]	I
PTB[d]				
1.55	95	16	0.62	I
1.55	95	83	1.08	I

[a] Measured dilatometrically.

[b] I, inert; A, air.

[c] Corresponds to 39% polymer yield.

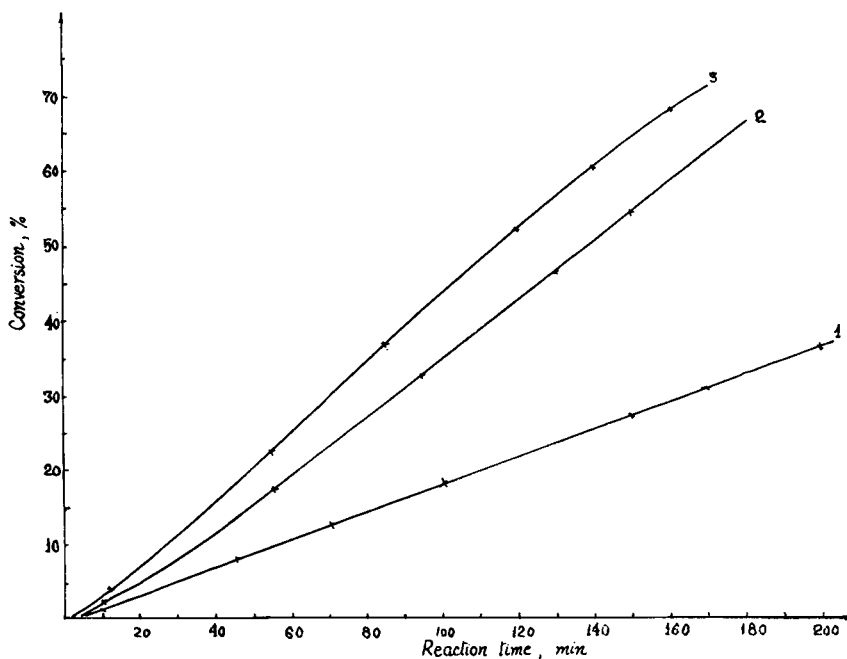[d] Polymerizations in ampules; instead of dilatometric conversions, polymer yields are given.

Fig. 3. Dilatometric curves of N-vinylcaprolactam bulk polymerization at 75°C. with different PBTB concentrations (%): (1) 0.5; (2) 1.5; (3) 2.0.
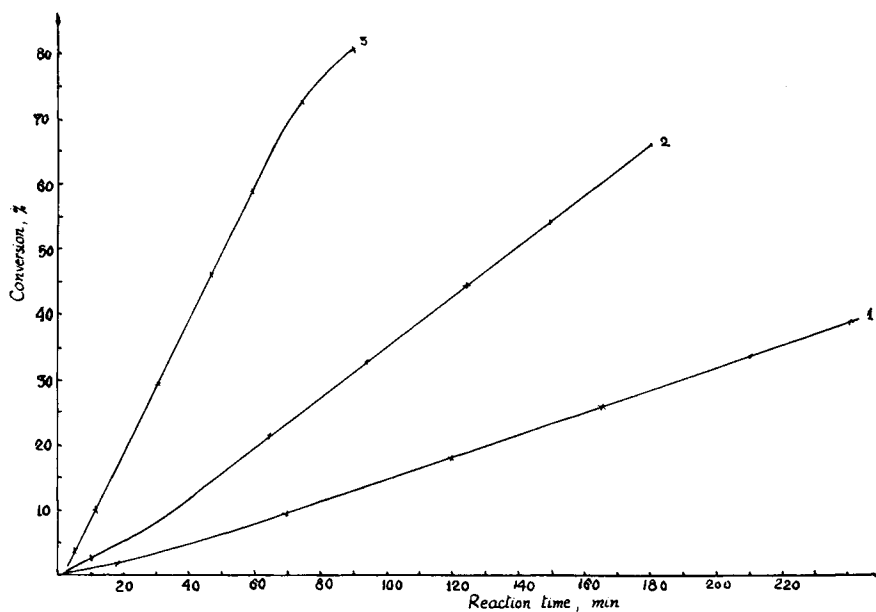
Fig. 4. Dilatometric curves of *N*-vinylcaprolactam bulk polymerization with 1.5% PTB at different temperatures (°C.): (*1*) 85; (*2*) 90; (*3*) 95.
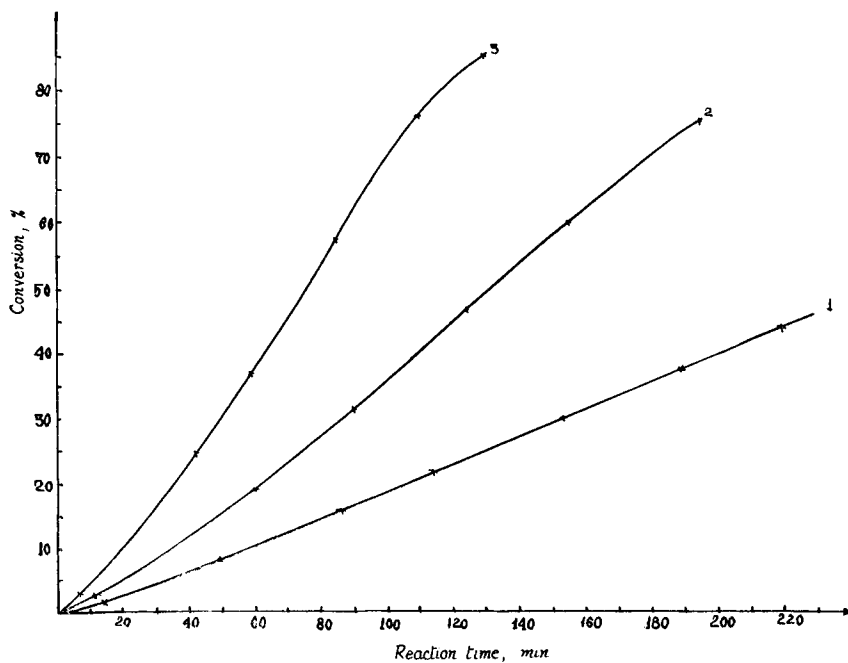

Fig. 5. Dilatometric curves of *N*-vinylcaprolactam bulk polymerization with 1.5% PBTB, at different temperatures (°C.): (*1*) 65; (*2*) 75; (*3*) 85.
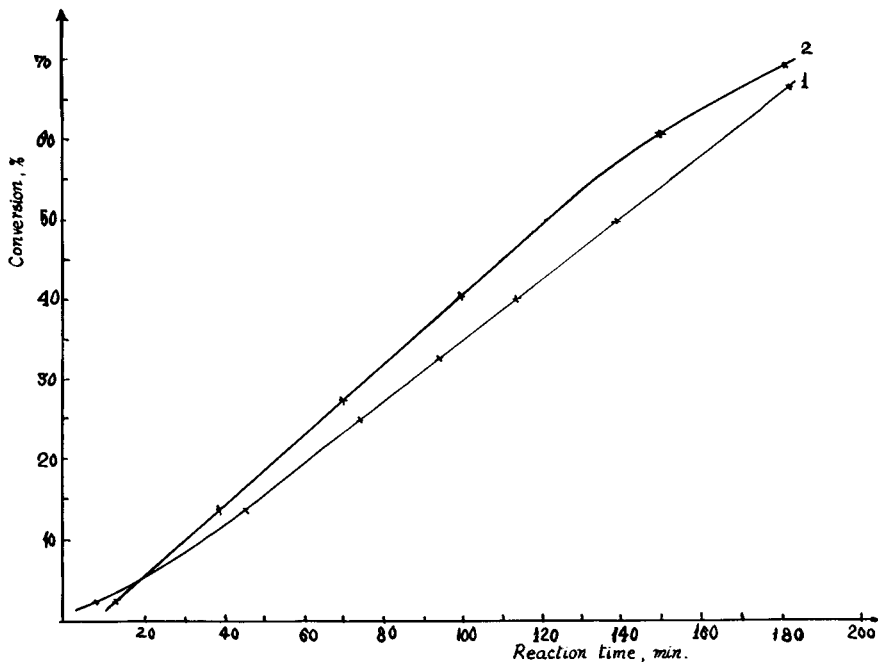
Fig. 6. Dilatometric curves of *N*-vinylcaprolactam bulk polymerization at 75°C. with different PBTB concentrations (%): (*1*) 1.5; (*2*) 21.4.

In the case of polymerization with AIBN the reaction rate is proportional to $[I].^{0.5}$ In the temperature range studied the classical kinetic equation for the overall reaction rate is applicable: $v = k[M][I]^{0.5}$. From experimental data were calculated $k_{70°C.} = 0.7 \times 10^{-1}$, $k_{75°C.} = 1.2 \times 10^{-1}$, and $k_{80°C.} = 1.9 \times 10^{-1}$ liter$^{0.5}$/mole$_i^{0.5}$ min. The activation energy of the reaction between 70 and 80°C. is 25 ± 2 kcal./mole.

As one can see in Figures 1 and 2, *N*-vinylcaprolactam bulk polymerization with initiator AIBN occurs without an induction period.

A study of the polymerization with different concentrations of PBTB (Fig. 3) also shows the dependence of the reaction rate on $[I]^{0.5}$.

In Figure 4 are presented the kinetic curves of *N*-vinylcaprolactam polymerization with PBTB at 65, 75, and 85°C. The form of the curves indicates that the temperature coefficient of the reaction increases appreciably with the temperature. That fact probably is due to the rate of initiator scission, which depends largely on the temperature.

In the case of PTB (Fig. 4) the temperature coefficient of the reaction is high, about 4 for $\Delta t = 10°C.$, but it remains practically constant in the temperature range studied.

Figures 1–5 show an unusual linearity of the kinetic curves up to high conversions: about 70% in the case of PBTB and PTB and about 55% in the case of AIBN. We consider this fact a result of compensation between two contrary tendencies: that of diminishing of the reaction rate, due to

the diminishing of the monomer concentration, and of increasing of the reaction rate, due to a weak gel effect. The presence of a weak Trommsdorf effect is indicated by some fragments of kinetic curves, which present a small increase in their slopes (Fig. 3, curves *2* and *3;* Figure 5, curves *1* and *2;* Figure 4, curves *1, 2,* and *3*), and by an increase in the polymer molecular weight during polymerization (some data are shown in Table III).

When PBTB was initiator, the polymers had lower molecular weight than when AIBN or PTB was used. At 85°C. and 1.5% initiator the polymers with PBTB had $[\eta] = 0.15$ dl./g., and those with PTB in the same conditions had $[\eta] = 0.66$ dl./g., that is, four times greater. It may be supposed that in the initiation of N-vinylcaprolactam polymerization with
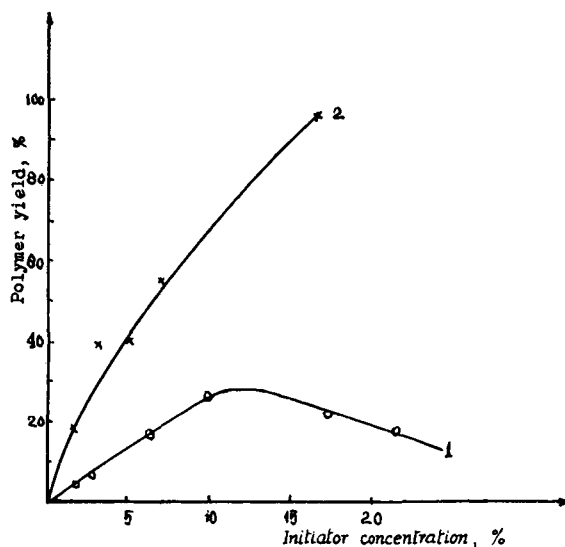

Fig. 7. Dependence of poly-N-vinylcaprolactam yield on initiator concentration: (*1*) PBTB, 65°C., 60 min.; (*2*) PTB, 90°C., 60 min.

PBTB chain-transfer reactions take place between the macroradicals and the initiator or some compounds formed by scission. Studying the influence of PBTB concentration on N-vinylcaprolactam conversion, on the polymer yield, and on the molecular weight, we observed that the reaction rate is about the same at 1.5% as at 21.4% initiator (Fig. 6); the polymer yield shows a maximum, after which considerable differences between the conversion and the yield appear (Table III and Fig. 7). The intrinsic viscosities diminish with increasing initiator concentration. These data permit us to draw the conclusion that PBTB acts, not only as initiator, but also as chain-transfer agent in N-vinylcaprolactam polymerization. At high PBTB concentrations the average molecular weight of the polymers formed becomes so low that a part of the polymer cannot be precipitated.

This fact explains the difference between conversions and yields and, consequently, the form of curve *1* in Figure 7.

At high concentrations PBTB not only shows activity as a chain-transfer agent but also produces a diminishing of the reaction rate.

When PTB was initiator, no diminishing of the polymer yield at high PTB concentrations was observed, nor was any diminishing of the reaction rate, as one may see in Figure 7, curve *2*. Therefore the PBTB behavior is due to the C_6H_5COO part of this molecule, a fact that is confirmed by the negative results obtained with benzoyl peroxide and lauroyl peroxide as initiators. In *N*-vinylcaprolactam polymerization at high PTB concentrations (over 10%) appreciable quantities of crosslinked polymers were formed.

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