

Radical Polymerization of *N*-Vinylcaprolactam in Homogeneous Solution. II

O. F. SOLOMON, D. S. VASILESCU, and V. TĂRĂRESCU,
*Laboratory of Macromolecular Chemistry, Polytechnic Institute of
Bucharest, Bucharest, Romania*

Synopsis

The polymerization of *N*-vinylcaprolactam in toluene, dioxane, chlorobenzene, dimethylformamide, and ethylene carbonate with various peroxides, perbenzoates and azobisisobutyronitrile as initiators at 60–80°C, was studied. Under these conditions azobisisobutyronitrile and *tert*-butyl perbenzoate have satisfactory activity as initiators. Under these conditions *N*-vinylcaprolactam polymerization in homogeneous solution is first order towards the monomer and 0.5 order towards the initiators.

Introduction

Few results have been published concerning the polymerization capacity of *N*-vinylcaprolactam with benzoyl peroxide at 55–60°C and azobisisobutyronitrile (AIBN).^{1–3} Studies of initiation of *N*-vinylcaprolactam polymerization with H₂O₂ have established that concurrently with the formation of some polymers of low molecular weight, a secondary reaction, i.e., the hydrolysis of *N*-vinylcaprolactam, leads to caprolactam and acetaldehyde.^{1,2}

Some copolymerizations^{1,2} and radiochemical polymerization⁴ of *N*-vinylcaprolactam have also been reported. The kinetics of solution polymerization has not been reported as far as the authors know. The results of this study are discussed.

Experimental

N-Vinylcaprolactam was synthesized by vinylation of caprolactam with acetylene, under pressure, in the presence of caprolactylpotassium. The monomer was isolated by vacuum distillation in argon, from the reaction mixture; bp – 96°C/4 mm Hg, $n_D^{40} = 1.5057$.³ Gas-liquid chromatographic analysis showed the product to be 99.5% pure.

In the presence of oxygen, the monomer, which was initially colorless, became yellow-brown after some time; this process is accelerated at increased temperatures and therefore, the kinetic activity of the monomer is lowered very much. For this reason, the monomer was stored in ampules under argon.

Solvents were purified by fractional distillation from guaranteed reagent grade, and finally dried over metallic sodium (for toluene) or calcium hydride (for dimethylformamide).

Polymerization was carried out in test tubes or dilatometers. Moisture was excluded from the system. The reagents were added with all-glass hypodermic syringes fitted with stainless steel needles. The air in the test tube was replaced with argon. The tube was sealed and put in a bath regulated at the desired temperature. The reaction mixture obtained by polymerization was poured into an excess of ether. The polymer was filtered off and dried *in vacuo* at 60°C for 24 hr.

Solutions 0.2% in toluene were used for the viscometric determination. The measurements were made with an Ubbelohde viscometer at 25°C. The values of intrinsic viscosities were calculated by the relation:⁵

$$[\eta] = \frac{\sqrt{2}}{c} \sqrt{\eta_{sp} - \ln \eta_{rel}}$$

Results and Discussions

The influence of some solvents used on the *N*-vinylcaprolactam (1 mole/l.) polymerization with 1% AIBN as initiator at 70°C, on the kinetics are given in Table I and Figure 1.

As is seen from the data in Table I, the conversions obtained in toluene, dioxane, and chlorobenzene were similar, but the polymers have different intrinsic viscosities.

After 10 hr, in ethylenecarbonate and dimethylformamide, no polymer precipitates on addition of diethyl ether. Table II presents the activity of different initiators for *N*-vinylcaprolactam polymerization in toluene. As one can see, AIBN is an effective initiator, and for the organic peroxides used, *tert*-butyl perbenzoate is also effective.

In Figure 2 is shown the influence of temperature on the polymerization kinetics of *N*-vinylcaprolactam with the *tert*-butyl perbenzoate.

It has been established that the conversion is considerably influenced by the temperature. In Figures 3–5 are presented data concerning the kinetics of the *N*-vinylcaprolactam polymerization in toluene with AIBN as initiator.

TABLE I

Solvent	Reaction time, hr	Conversion %	$[\eta]$, dl/g
Toluene	2	51.5	0.12
Dioxane	2	58.2	0.14
Chlorobenzene	2	59.1	0.24
Dimethylformamide	10	—	—
Ethylene carbonate	10	—	—

TABLE II

Initiator	Monomer, mole/l.	Initiator, %	Temp, °C	Time, hr	Conversion, %	$[\eta]$, dl/g
AIBN	1	0.5	70	2	19.7	0.14
	1	0.5	80	2	34.6	0.10
	1	0.5	90	2	60.3	0.10
<i>tert</i> -Butyl perbenzoate	4	1.0	70	0.25	45.0	0.25
	4	2.2	80	3	61.8	0.24
	4	2.2	90	3	78.5	0.11
	4	2.2	100	2	81.0	—
Di- <i>tert</i> -butyl peroxide	4	1.7	80	6	0	—
	4	1.7	90	6	0	—
	4	1.7	100	6	26.4	0.20
	4	2.0	80	6	0	—
Benzoyl peroxide Lauroyl peroxide	4	2.0	80	6	11.8	0.14
	4	2.0	100	6	12.3	0.12
Cyclohexanone peroxide	4	2.2	90	6	29.0	0.10

The influence of the monomer concentration on the conversion is shown in Figure 3. It was established that the reaction rate is directly proportional to the monomer concentration; on polymerization of *N*-vinylcaprolactam at high concentration (4 mole/l.), after a certain conversion, precipitation of the polymer occurs.

The way in which the conversion depends on the initiator concentration (using the integral method) leads us to conclusion that the reaction rate is proportional to $(I)^{0.5}$.

The effect of reaction temperature on the conversion is shown in Figure 5.

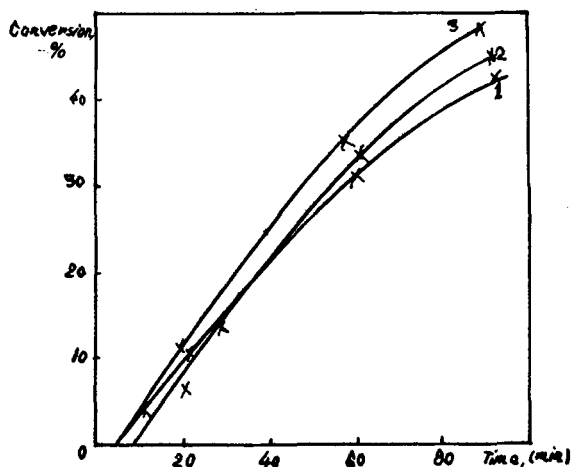


Fig. 1. *N*-Vinylcaprolactam polymerization (1 mole/l.) with AIBN at 75°C: (1) in toluene; (2) in dioxane; (3) in chlorobenzene.

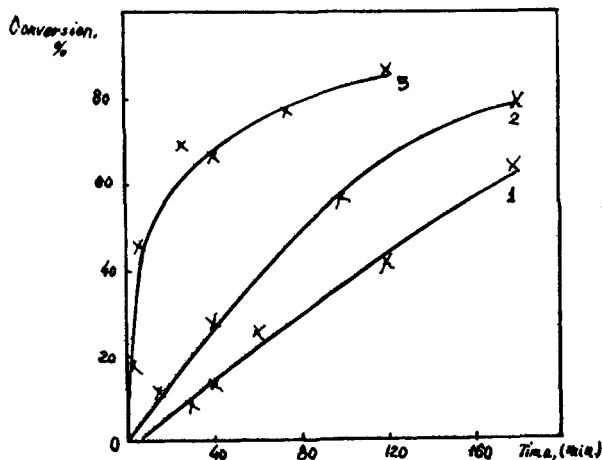


Fig. 2. *N*-Vinylcaprolactam polymerization (4 mole/l.), with 2.24% *tert*-butyl perbenzoate with toluene as solvent: (1) at 80°C; (2) at 90°C; (3) at 100°C.

TABLE III

Polymerization temperature,	
°C	$K, l.^{0.5}/mole^{0.5}\text{-sec}$
60	0.48×10^{-3}
70	0.10×10^{-3}
80	2.71×10^{-3}

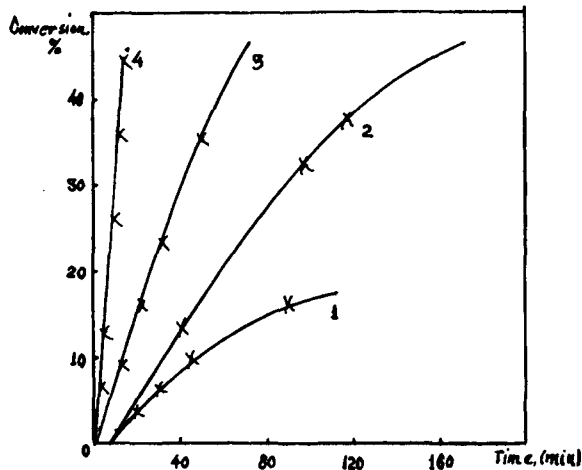


Fig. 3. *N*-Vinylcaprolactam polymerization with toluene as solvent with 0.5% AIBN at 70°C and various monomer concentrations: (1) 0.5 mole/l.; (2) 1 mole/l.; (3) 2 mole/l.; (4) 4 mole/l.

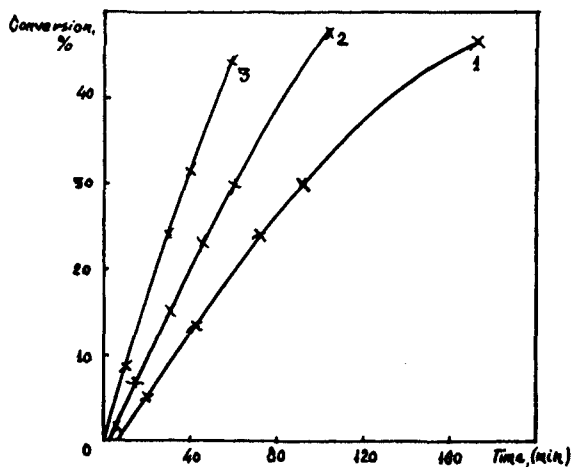


Fig. 4. *N*-Vinylcaprolactam polymerization (1 mole/l.) with toluene as solvent at 70°C and various AIBN concentrations: (1) 0.5%; (2) 1%; (3) 2%.

The values for the rate constant of this process obtained are shown in Table III. In Table IV are shown the intrinsic viscosity for polymers obtained in the polymerization with 0.5% AIBN at different temperatures.

TABLE IV

Polymerization temperature, °C	$[\eta]$, dl/g
60	0.19
70	0.14
80	0.10
90	0.09

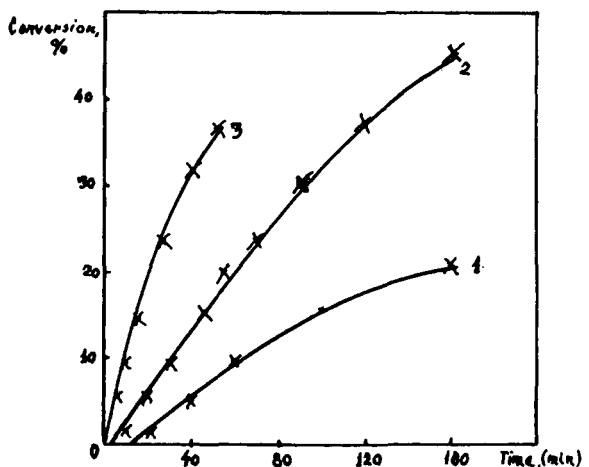


Fig. 5. *N*-Vinylcaprolactam polymerization (1 mole/l.), with 0.5% AIBN and toluene as solvent: (1) at 60°C; (2) at 70°C; (3) at 80°C.

Conclusions

The polymerization of *N*-vinylcaprolactam in the presence of solvents (i.e., chlorobenzene, dioxane, toluene) follows the general law of the radical polymerization. The data given by Shostakovsky^{1,2} concerning the lack of initiation with benzoyl peroxide have been confirmed, but other peroxides used for the first time for this monomer permit polymerization even at temperatures lower than 100°C.

At high concentrations of the monomer, after a certain conversion, the solution polymerization in toluene polymer precipitates from the mixtures; at the same time, an autoacceleration process occurs in the presence of the gel. It was experimentally established that in dimethylformamide and ethylene carbonate one can not obtain polymers which can be precipitated with diethyl ether; this fact may be attributed to the very intense chain-transfer with the solvent.

References

1. M. F. Shostakovsky and N. A. Medzihovskaya, *Izf. Akad. Nauk SSSR, Otd Khim. Nauk*, **1952**, 682, 690; *ibid.*, **1957**, 1457.
2. M. F. Shostakovsky and F. P. Sidelkovskaya, *Vysokomol. Soedin.*, **3**, 976 (1961).
3. O. F. Solomon, M. Corciovei, and C. Boghină, *J. Appl. Polym. Sci.*, in press.
4. Gy. Hardy, K. Nytray, I. Varga, G. Kovacs, and N. Fedorova, in *Macromolecular Chemistry (J. Polym. Sci. C, 4)*, M. Magat, Ed., Interscience, New York, 1963, p. 923.
5. O. F. Solomon and I. Z. Ciută, *J. Appl. Polym. Sci.*, **6**, 683 (1962).

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