

the Drude equation shows that the values of λ_0 for the monomer and both polymers differ little, but the value of A for the radical polymer is lower than that for the anionic polymer. A decrease in the constant A and a shift of the peak toward the shortwave region of the spectrum is an indication of stereoregularity in the polymer structure.

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THE COPOLYMERIZATION OF N-VINYL LACTAMS WITH ALKYL VINYL ETHERS*

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MUCH attention is being given to polymers of N-vinyl lactams because they possess a number of interesting properties. In recent years intensive studies concerned with modification of the properties of these polymers by copolymerization with other unsaturated compounds have been initiated. However published information on this question is very limited and is found mainly in the patent literature. For example copolymers have been obtained from vinylpyrrolidone with the vinyl esters of higher fatty acids [1], unsaturated organosilicon compounds [2], sodium ethylenesulphonate [3-5], vinyl carbonate [6], vinylsulphonic acid [7], β -(N-pyrrolidonyl)ethylvinyl sulphide [8], acrylonitrile and methyl methacrylate [9, 10] and with other monomers [11-15].

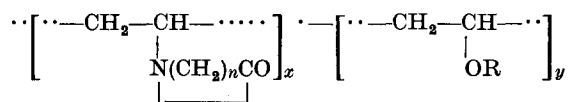
The preparation of a block copolymer of vinylpyrrolidone and dextran has been described [16]. There are still fewer known examples of copolymers of vinylcaprolactam. In the present work a study was made of the copolymeriza-

* Vysokomol. soyed. **6**: No. 9, 1585-1590, 1964.

tion of N-vinylpyrrolidone (VP) and N-vinylcaprolactam (VC) with vinyl ethers. The reaction was studied with ethyl vinyl ether (EV), isopropyl vinyl ether (IPV) and *n*-butyl vinyl ether (BV) as examples. The copolymers of the above monomer pairs could be of practical interest. For example the homopolymers of vinyl lactams are brittle products, easily breaking down to powders, and the vinyl ether homopolymers are semi-liquid or elastic, solid masses. Moreover vinyl lactam-vinyl ether copolymers could be of interest in medicine. It is well known that the homopolymers of some of the above monomers have already found application as medical preparations—polybutylvinylether is a medical balsam and solutions of polyvinylpyrrolidone are used as synthetic substitutes for blood plasma.

Azobisisobutyronitrile (ADIB) was used as the initiator for copolymerization of the vinyl lactams with vinyl ethers. It has been found that vinyl lactams do not form polymers in the presence of benzoyl peroxide but they polymerize readily in the presence of ADIB [17]. In contrast to the vinyl lactams, vinyl ethers do not satisfactorily form homopolymers by free-radical initiation. It has been shown that in equimolar proportions benzoyl peroxide adds to vinyl ethers, forming compounds of the type $C_6H_5COOCH_2CH(OR)OCOC_6H_5$ [18]. When vinyl ethers are heated with catalytic quantities of benzoyl peroxide only oligomers of molecular weight of about 1000 are obtained [19]. ADIB also converts vinyl ethers only to polymers of low molecular weight [20], and the yield of these is not greater than 10–12%. However vinyl ethers undergo free-radical copolymerization, forming products containing up to 50% of vinyl ether units [21].

In the present work various initial monomer ratios were used in order to establish the basic relationships and character of the copolymerization process for the given pairs of monomers. The structure of the copolymers may be represented as follows:



where $n=3$ or 5 and $R=C_2H_5$, *iso*- C_3H_7 or *n*- C_4H_9 .

The main results of the study are presented in tabular form. Table 1 shows the yield and composition of copolymers of VP.

It is seen from Table 1 that VP is more reactive in copolymerization than the vinyl ethers. The copolymers are richer in VP than the initial monomer mixture. The highest content of VP units in the copolymers is ~88 moles% and the content of vinyl ether units is never greater than 55 moles%. The difference in the reactivity of the monomers also affects the yield of the copolymers. The highest yield is obtained when VP is polymerized alone. As the vinyl ether content of the monomer mixture increases the yield of copolymer falls. A similar effect was found in the copolymerization of vinyl ethers with VC. The highest

TABLE 1. COPOLYMERIZATION OF VP (M_1) WITH EV, IPV AND BV (M_2)

M_2	Mole fraction of M_1 in initial mixture	Yield of polymer or copolymer, %	Nitrogen content* of copolymer, %	Mole fraction of m_1 in copolymer	Mol. wt. of copolymer
EV	0.10	18.4	7.39	0.455	550-600
	0.25	36.8	9.0	0.618	—
	0.50	49.9	10.0	0.714	—
	0.75	59.3	10.01	0.716	—
	0.90	63.1	11.05	0.822	—
IPV	1.00	67.5	12.24	1.00	—
	0.10	8.9	7.81	0.555	—
	0.25	9.8	9.15	0.672	—
	0.50	63.0	10.07	0.754	900-1000
	0.75	76.6	10.08	0.756	—
BV	1.00	67.5	12.24	1.00	—
	0.10	4.4	8.7	0.631	—
	0.25	21.9	9.89	0.713	—
	0.50	56.4	10.02	0.721	700-750
	0.75	83.7	11.06	0.795	—
	0.90	85.1	12.06	0.873	—
	1.00	67.5	12.24	1.00	—

*The nitrogen content quoted is the mean of two determinations.

TABLE 2. COPOLYMERIZATION OF VC (M_1) WITH EV, IPV AND BV (M_2)

M_1	Mole fraction of M_1 in initial mixture	Yield of polymer or copolymer, %	Nitrogen content of copolymer, %	Mole fraction of m_1 in copolymer	Mol. wt. of copolymer
EV	0.10	19.3	6.42	0.481	850-1180
	0.25	45.0	7.54	0.607	800
	0.50	68.7	8.59	0.753	700
	0.75	70.3	8.87	0.795	750
	1.00	61.9	10.09	1.00	—
IPV	0.10	7.7	6.13	0.491	1500
	0.25	42.4	7.19	0.608	900-1200
	0.50	66.0	8.41	0.735	1000-1100
	0.75	73.5	9.3	0.884	—
	0.90	74.2	9.99	0.988	—
BV	1.00	61.9	10.09	1.00	—
	0.10	8.3	5.99	0.515	850-900
	0.25	37.6	7.52	0.679	850-1000
	0.50	57.5	8.76	0.829	850-900
	0.75	68.4	8.87	0.844	900-950
	0.90	77.7	9.14	0.886	—
	1.00	61.9	10.09	1.00	—

proportion of VC units in the copolymers was ~ 99 moles % and of vinyl ether units not more than 52 moles % (Table 2).

The fact that copolymerization between the vinyl lactams and vinyl ethers has occurred is confirmed by the solubility of the products (see Table 3).

The copolymers are not soluble in either diethyl ether or in water. On the other hand vinyl ether homopolymers are readily soluble in ether and vinyl lactam homopolymers are readily soluble in water.

TABLE 3. SOLUBILITY OF HOMOPOLYMERS AND OF COPOLYMERS OF VP AND VC WITH ALKYL VINYL ETHERS

Composition of initial monomer mixture (moles %)	Solubility*								
	Ace-tone	Ben-zene	Chlo-ro-form	CCl ₄	Etha-nol	Diethyl ether	Petro-leum ether	Dime-thyl-form-amide	Water
VP homopolymer	s	s	s	s	s	i	i	s	s
EV homopolymer	s	s	s	s	s	s	s	s	i
25% VP + 75% EV	s	s	s	s	s	i	i	s	i
75% VP + 25% EV	s	s	s	s	s	i	i	s	i
IPV homopolymer	s	s	s	s	s	s	s	s	i
25% VP + 75% IPV	s	s	s	s	s	i	i	s	i
75% VP + 25% IPV	p.s.	p.s.	p.s.	p.s.	p.s.	i	i	s	i
BV homopolymer	p.s.	s	p.s.	p.s.	s	s	i	s	i
25% VP + 75% BV	s	s	s	s	s	i	i	s	i
75% VP + 25% BV	sw.	sw.	sw.	sw.	sw.	i	i	s	i
VC homopolymer	s	s	s	s	s	i	i	s	s
25% VP + 75% EV	s	s	s	s	s	i	i	s	i
75% VC + 25% EV	s	s	s	s	s	i	i	s	i
25% VC + 75% IPV	s	s	s	s	s	i	i	s	i
75% VC + 25% IPV	p.s.	p.s.	p.s.	p.s.	p.s.	i	i	s	i
25% VC + 75% BV	s	s	s	s	s	i	i	s	i
75% VC + 25% BV	s	s	s	s	s	i	i	s	i

*Abbreviations: s — soluble; i — insoluble; sw — swells; p.s. — partially soluble.

The molecular weights of some of the copolymers were determined (cryoscopically in benzene). This showed that the copolymers are of low molecular weight, which varies between 500 and 1500.

The relative viscosity of all the copolymers was determined at 20° in dimethylformamide (DMF) (this was found to be a common solvent for all the copolymers) (see Table 4).

As the proportion of vinyl lactam units in the copolymers increases the relative viscosity increases, indicating some increase in molecular weight.

The effect of time on the yield and composition of the copolymers was studied in the case of VP-BV copolymers (Table 5).

It was found that the yield of copolymers increases with increasing reaction time but the composition of the product changes little.

TABLE 4. VISCOSITY IN DMF OF COPOLYMERS OF VP AND VC WITH VINYL ETHERS
(0.5 g/100 ml of solvent)

Composition of initial monomer mixture, moles %	η_r at 20°	Composition of initial monomer mixture, moles %	η_r at 20°
VP homopolymer	2.513*	VC homopolymer	3.358*
10% VP+90% EV	1.1103	10% VC+90% EV	1.0910
25% VP+75% EV	1.1516	25% VC+75% EV	1.1718
50% VP+50% EV	1.2939	50% VC+50% EV	1.2641
10% VP+90% IPV	1.0703	75% VC+25% EV	1.2134
25% VP+75% IPV	1.0149	50% VC+50% IPV	1.4008
50% VP+50% IPV	1.3406	75% VC+25% IPV	1.4801
10% VP+90% BV	1.0451	10% VC+90% BV	1.0544
25% VP+75% BV	1.2510	25% VC+75% BV	1.0805
50% VP+50% BV	1.5611	50% VC+50% BV	1.2018
75% VP+25% BV	1.6001	75% VC+25% BV	1.1601

* These viscosities were determined in ethanol solution at a concentration of 1g/100 ml of solvent.

TABLE 5. EFFECT OF REACTION TIME IN THE COPOLYMERIZATION OF VP (M_1) WITH BV, ON THE YIELD AND COMPOSITION OF THE COPOLYMERS

Mole fraction of M_1 in initial mixture	Copolymerization time, hours	Yield of copolymer, %	Nitrogen content of copolymer, %	Mole fraction of m_1 in copolymer
0.50	0.5	10.1	11.24	0.808
0.50	1.0	10.9	11.13	0.802
0.50	2.0	27.9	Not determined	
0.50	3.0	36.0	Ditto	
0.50	4.0	43.8	"	
0.50	5.0	49.7	10.99	0.793
0.40	0.5	3.3	11.92	0.861
0.40	1.0	5.1	11.15	0.701
0.40	2.0	19.8	11.04	0.724
0.40	5.0	39.9	Not determined	
0.40	10.0	43.8	Ditto	
0.40	30.0	44.1	11.51	0.905

In order to determine the reactivity ratios of the various monomer pairs copolymerization was carried out to low degrees of conversion. The results are presented in Table 6.

TABLE 6. EXPERIMENTAL DATA FOR DETERMINATION OF REACTIVITY RATIOS

Mole fraction of monomers in initial mixture			Yield, %	N content %	Concentration of monomers, mmoles			
					[M ₁]	[M ₁]	[M ₂]	[M ₂]
VP (M ₁)	IPV (M ₂)	BV (M ₂)						
0.1	0.9	—	8.9	7.81	3.96	2.34	35.99	34.37
0.5	0.5	—	19.57	11.69	50.65	48.49	50.65	48.50
0.9	0.1	—	18.91	12.03	82.87	66.85	9.15	7.89
0.1	—	0.9	4.4	8.7	3.32	2.52	30.06	29.55
0.4	—	0.6	5.1	11.15	79.99	73.24	120.31	117.11
0.75	—	0.25	87.7	11.06	29.96	9.79	10.8	5.11
VC (M ₁)	IPV (M ₂)	BV (M ₂)						
0.1	0.9	—	7.7	6.13	6.21	4.68	44.93	42.84
0.5	0.5	—	2.13	9.73	44.31	43.33	44.31	43.66
0.9	0.1	—	2.54	10.08	84.22	82.51	7.43	6.73
0.1	—	0.9	8.3	5.99	4.02	2.73	36.44	34.74
0.5	—	0.5	1.33	9.53	41.82	40.95	41.82	41.63
0.9	—	0.1	7.47	9.91	66.53	61.29	7.39	7.19

The reactivity ratios were determined graphically by means of the Mayo and Lewis integral equation [22] (see Table 7).

TABLE 7. MONOMER REACTIVITY RATIOS

M ₁	r ₁	M ₂	r ₂	M ₁	r ₁	M ₂	r ₂
VP	1.68	IPV	0	VC	1.88 ± 0.02	IPV	0
VP	2.97 ± 0.01	BV	0	VC	1.39 ± 0.01	BV	0

The reactivity ratios of these monomers confirm that VP and VC are more reactive than IPV and BV. For any ratio of monomers in the initial mixture the copolymers are richer in VP and VC.

EXPERIMENTAL

The monomers were freshly distilled before use and had the following constants: N-vinyl pyrrolidone—b. p. 71–72°/2.5 mm, n_D^{20} 1.5117; d_4^{20} 1.0458; N-vinylcaprolactam—b.p. 94–95°/4 mm; n_D^{20} 1.5135; d_4^{20} 1.0290; ethyl vinyl ether—b.p. 36.0°, n_D^{20} 1.3779; d_4^{20} 0.7531; isopropyl vinyl ether—b.p. 55.0–55.5°; n_D^{20} 1.3862; d_4^{20} 0.7520; n-butyl vinyl ether—93.7–93.8°; n_D^{20} 1.4026; d_4^{20} 0.7792. The ADIB was twice recrystallized from methanol. Polymerization was carried out in the presence of ADIB (0.2% on the total weight monomers, total monomer charge 5 g) at 60 ± 1° for 72 hours in sealed ampoules that were swept out with nitrogen before being sealed. The copolymers were reprecipitated twice and washed with the precipitant until the washings gave no reaction for double bonds with bromine. The solvent was ethanol or benzene and the precipitant was petroleum ether. The precipitated copolymers were then dried to constant weight (at 10⁻³ mm) and analysed for nitrogen.

The composition of the copolymer was calculated from the nitrogen content. The results are presented in Tables 1 and 2.

The practical application of these copolymers is now being studied.

CONCLUSIONS

(1) The copolymerization of N-vinylpyrrolidone (VP) and N-vinylcaprolactam (VC) with alkyl vinyl ethers, initiated by azobisisobutyronitrile, has been studied.

(2) Copolymers of VP and VC with ethyl vinyl ether (EV), isopropyl vinyl ether (IPV) and *n*-butyl vinyl ether have been prepared and conditions for the production of copolymers rich in the N-vinyl lactam units were found.

(3) The relative viscosities and solubilities of the copolymers were determined.

(4) The reactivity ratios of the following pairs of monomers were determined: VP-IPV ($r_1=1.68$; $r_2=0$); VP-BV ($r_1=2.97\pm 0.01$, $r_2=0$), VC-IPV ($r_1=1.88\pm 0.02$, $r_2=0$), VC-BV ($r_1=1.39\pm 0.01$; $r_2=0$).

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