

# COPOLYMERIZATION OF N-VINYLLACTAMS WITH VINYLPHENYL AND VINYLCYCLOHEXYL ETHERS\*

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PREVIOUSLY [1] we studied the copolymerization of N-vinylpyrrolidone (VP) and N-vinylcaprolactam (VC) with vinylalkylethers of the overall structure  $\text{CH}_2=\text{CHOR}$  ( $\text{R}=\text{C}_2\text{H}_5$ ; *iso*- $\text{C}_3\text{H}_7$ ; *n*- $\text{C}_4\text{H}_9$ ). We felt it would be interesting to extend this study to the example of vinylaryl ethers and ethers of cyclic alcohols. As the representative of the first group of compounds, we chose vinylphenyl ether (VPE) and for the second group, vinylcyclohexyl ether (VCH). As initiator we used azobisisobutyronitrile. Parallel copolymerization experiments were performed with vinylactam and VPE and VCH using another initiator, benzoyl peroxide.

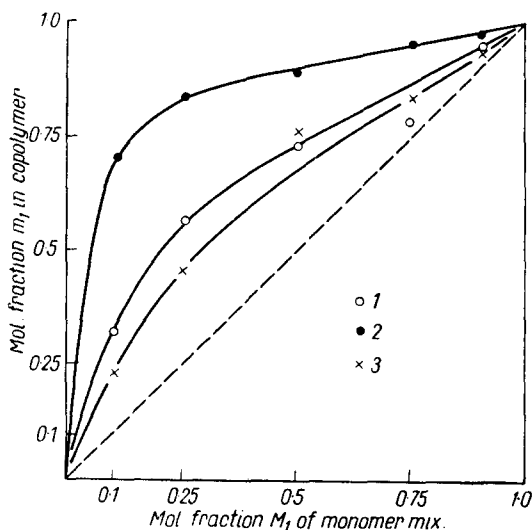
There is a mention in the literature on the copolymerization of VP and VPE with benzoyl peroxide [2]. When our monomers were heated with benzoyl peroxide we did not find either formation of homopolymers or copolymers. In this work vinylactams were copolymerized with VPE and VCH in various different ratios in the original mix. Moreover, in one series of experiments the process was continued to greater stages of conversion in order to separate and study the products; in the other the polymerization was interrupted at an early state of conversion in order to determine  $r_1$  and  $r_2$  the relative activities. Comparing the results with those obtained in the copolymerization of vinylactams with vinylalkyl ethers [1], it is evident that in both cases the copolymers are enriched with vinylactam chains as compared with the monomer mix, this enrichment being more definite with the vinylalkyl ethers than the VPE. In copolymerization with vinylactams the vinylcyclohexyl ethers behave in the same way as the vinylalkyl ethers.

The findings of the copolymerization of vinylactams with VPE and VCE are shown in Table 1 and the Figure. As the vinylactam concentration increased so also did the concentration of their units in the copolymer. In copolymerization with VCE no copolymers were formed which contained more than 50% units of this monomer. But with VPE, where its concentration in the starting monomer mix was high (90 mol.%) the resultant copolymers had 70–80 mol.% VPE units. The same kind of thing occurred with the copolymerization of VC and VPE.

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The solubility of the products further confirmed the copolymerization of VP and VC with VPE and VCE.

The molecular weight was determined bioscopically in benzene for a number of copolymer specimens, and found to range between 1000 and 1500. Superficially the product copolymers VP-VPE, VP-VCE and VC-VPE are ivory coloured powders. If left for a while they start to melt. They seem to be slightly hygroscopic. They form brittle films and have only weak adhesion to glass, wood, paper or metal.



Composition of the copolymers VP-VPE (1), VP-VCH (2) and VC-VPE (3).

To find the relative activity of the radicals of our pairs of monomers, the copolymerization reaction was conducted to slight degrees of conversion. The experimental findings are shown in Table 2, from which  $r_1$  and  $r_2$  were calculated graphically using the integral equation of Mayo and Lewis [3]. The relative radical activities found were as follows: VP-VPE  $r_1=4.43 \pm 0.001$ ;  $r_2=0.22 \pm 0.001$ ; VP-VCE  $r_1=3.84$ ,  $r_2=0$ ; VC-VPE  $r_1=2.53 \pm 0.03$ ,  $r_2=0.39 \pm 0.3$ .

These figures show that VP and VC are more active components than VPE and VCE. The copolymers will be enriched with VP and VC chains whatever the ratio of monomers in the original mix.

After finding  $r_1$  and  $r_2$  for the system VP-VPE and VC-VPE, we went on to find  $Q$  the specific activity and  $e$  the polarity of the monomers VC and VPE. These figures are not available in the literature. The  $Q$  and  $e$  values to hand were calculated on the example of copolymerization of the following pairs: VP-styrene [4, 5], VP-MMA [5], VP-vinyl chloride [6], VP-vinylethylurethane [7]. We used the data of [4-7] to calculate the mean  $Q$  and  $e$  values and found them to be  $Q=0.096$  and  $e=-1.27$ . Using these figures and those obtained for

TABLE 1. COPOLYMERIZATION OF VP AND VC WITH VPE AND VCH

| Monomers | VP or VC molar fraction in original mix $M_1$ | Yield of polymers or copolymers, % | N concentration of copolymer, % | VP or VC molar fraction in copolymer, $m_1$ | Molecular weight |
|----------|---|------------------------------------|---------------------------------|---|------------------|
| VP-VPE   | 0.10  | 3.6                                | 3.6                             | 0.302                                       | —                |
|          | 0.25  | 9.6                                | 6.86                            | 0.563                                       | 900-1000         |
|          | 0.50  | 20.0                               | 8.95                            | 0.731                                       | —                |
|          | 0.75  | 38.6                               | 9.64                            | 0.782                                       | 1210-1250        |
|          | 0.90  | 53.9                               | 11.02                           | 0.942                                       | —                |
|          | 1.00  | 67.5                               | 12.24                           | 1.00  | —                |
| VP-VCH   | 0.10  | 4.8                                | 8.58                            | 0.708                                       | —                |
|          | 0.25  | 10.1                               | 10.01                           | 0.848                                       | —                |
|          | 0.50  | 23.9                               | 11.00                           | 0.887                                       | 1100-1190        |
|          | 0.75  | 43.9                               | 11.92                           | 0.953                                       | 1270-1300        |
|          | 0.90  | 56.3                               | 12.02                           | 0.966                                       | —                |
|          | 1.00  | 67.5                               | 12.24                           | 1.00  | —                |
| VC-VPE   | 0.10  | 2.5                                | 2.66                            | 0.237                                       | —                |
|          | 0.25  | 6.0                                | 5.04                            | 0.464                                       | 800-900          |
|          | 0.50  | 17.3                               | 8.08                            | 0.780                                       | 980-1100         |
|          | 0.75  | 35.1                               | 8.47                            | 0.829                                       | 1250-1310        |
|          | 0.90  | 50.4                               | 9.25                            | 0.908                                       | 1450-1490        |
|          | 1.00  | 61.9                               | 10.09                           | 1.00  | —                |

TABLE 2. EXPERIMENTAL FINDINGS FOR DETERMINATION OF RELATIVE ACTIVITIES

| Molar fraction of monomers in original mix |      | Yield, % | N concentration, % | Copolymer, composition, molar fractions |       | Concentration of monomers, m mole |         |           |         |
|--|------|----------|--------------------|---|-------|-----------------------------------|---------|-----------|---------|
|  |      |          |                    |   |       | $[M_1^0]$                         | $[M_1]$ | $[M_2^0]$ | $[M_2]$ |
| VP   | VPE  |          |                    | VP                                      | VPE   | VP                                |         |           |         |
| 0.1  | 0.9  | 3.6      | 3.6                | 0.302                                   | 0.698 | 4.14                              | 3.69    | 37.79     | 36.71   |
| 0.25                                       | 0.75 | 9.6      | 6.86               | 0.563                                   | 0.437 | 10.61                             | 8.14    | 31.79     | 30.04   |
| 0.75                                       | 0.25 | 16.6     | 11.57              | 0.924                                   | 0.076 | 66.13                             | 61.36   | 22.05     | 21.11   |
| VP   | VCH  |          |                    | VP                                      | VCH   | VP                                |         | VCH       |         |
| 0.1  | 0.9  | 4.8      | 8.58               | 0.708                                   | 0.292 | 3.96                              | 2.43    | 36.21     | 35.59   |
| 0.25                                       | 0.75 | 10.1     | 10.01              | 0.815                                   | 0.185 | 9.12                              | 6.57    | 30.74     | 29.87   |
| 0.9  | 0.1  | 15.3     | 11.85              | 0.945                                   | 0.055 | 79.89                             | 68.65   | 8.88      | 8.21    |
| VC   | VPE  |          |                    | VC                                      | VPE   | VC                                |         | VPE       |         |
| 0.1  | 0.9  | 2.5      | 2.66               | 0.237                                   | 0.763 | 3.31                              | 3.17    | 37.04     | 36.37   |
| 0.25                                       | 0.75 | 6.0      | 5.04               | 0.464                                   | 0.536 | 10.05                             | 9.06    | 29.96     | 28.63   |
| 0.75                                       | 0.25 | 4.9      | 8.47               | 0.814                                   | 0.186 | 56.11                             | 53.23   | 18.31     | 17.55   |

the copolymerization of VP and VPE, we calculated  $Q$  and  $e$  for VPE with the Alfrey and Price equation [8];  $Q=0.027$ ,  $e=-1.43$ . Then, using the findings of the VC-VPE copolymerization we found  $Q$  and  $e$  for VC;  $Q=0.081$ ,  $e=-1.55$ . These figures can be used for a rough determination of the relative activities for the copolymerization of VC and VPE with other vinyl monomers without any preliminary experimental investigations.

#### EXPERIMENTAL

As starting materials we used the following, freshly distilled: N-vinylpyrrolidone, b.p. 71–72°/2.5 mm,  $n_D^{20}$  1.5117,  $d_4^{20}$  1.0468; N-vinylcaprolactam, b.p. 94–95°/4 mm,  $n_D^{20}$  1.5135,  $d_4^{20}$  1.0290; vinylphenyl ether, b.p. 155–156°/750 mm,  $n_D^{20}$  1.5225,  $d_4^{20}$  0.9770; vinylcyclohexyl ether b.p. 154–154.5°/750 mm,  $n_D^{20}$  1.5080,  $d_4^{20}$  0.8330. The asobisisobutyronitrile was twice recrystallized from methanol. The polymerization was performed in ampoules at  $60 \pm 1^\circ$  for 72 hr in the presence of 0.2% of the initiator. The starting monomers were taken in various different molar ratios (total amount of mix approx. 5 g). Control experiments in the polymerization of the original monomers were set up under exactly the same conditions. The copolymers of VP and VC with VPE and VCE were dissolved in ethanol or benzene and precipitated with petroleum ether. Then they were dried to constant weight at  $10^{-3}$  mm, analysed for nitrogen content and from this figure their composition was calculated. The findings are shown in Table 1. The relation between the concentrations of the original monomers and the amount of monomer units in the copolymer can be seen from the Figure. The synthesized copolymers are insoluble in water, diethyl and petroleum ethers, soluble in acetone, benzene, chloroform, carbon tetrachloride and dimethylformamide.

#### CONCLUSIONS

(1) N-vinylpyrrolidone (VP) and N-vinylcaprolactam have been copolymerized with vinylphenyl ether (VPE) and vinylcyclohexyl ether (VCH) in the presence of asobisisobutyronitrile. New copolymers have been synthesized.

(2) The copolymer yield has been found to rise with the N-vinylactam concentration of the original mix. The copolymers contain more N-vinylactam units than does the monomer mix.

(3) The relative activities have been determined and found to be as follows: VP-VPE  $r_1=4.43 \pm 0.001$ ,  $r_2=0.22 \pm 0.001$ ; VP-VCH  $r_1=3.84$ ,  $r_2=0$ ; VC-VPE  $r_1=2.53 \pm 0.03$ ,  $r_2=0.39 \pm 0.003$ . The activity factors have been calculated for VC, as  $Q=0.081$  and  $e=-1.55$ ; and for VPE  $Q=0.027$  and  $e=-1.43$

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