Temperature Dependence of Copolymerization*

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During the last five years a considerable amount of experimental material has been accumulated on the rate constant ratios of copolymerization.¹⁻³ Most of this work has been carried out at one temperature, thus giving us no information concerning the temperature dependence of the copolymerization ratios. The temperature dependence of these ratios is of considerable interest since it represents the difference of the energies of activation of the respective addition reactions, and thus gives the lower limit of those values:

$$r = k_{aa}/k_{ab} = Ke^{-(E_{aa}-E_{ab})/RT}$$

The present paper gives the results obtained with the three monomer pairs styrene-dichlorostyrene, styrene-acrylonitrile, and dichlorostyrene-acrylonitrile, in the temperature range between 38.5 and 86.5 °C.

EXPERIMENTAL PROCEDURE

The styrene was obtained from the Monsanto Chemical Co. and was used without further purification after it had been determined that no polymer was present. The acrylonitrile was obtained from the American Cyanamid Company and was used without further purification after it had been determined that no polymer was present. The dichlorostyrene was obtained from Dr. T. Alfrey, Polytechnic Institute of Brooklyn. It was distilled under vacuum from room temperature to liquid nitrogen temperature.

The monomers were added to cleaned test tubes along with 0.1 mole per cent benzoyl peroxide. The tubes were sealed under vacuum and placed in constant-temperature baths in which the temperature was not allowed to vary more than 0.2 °C. After the polymerization had progressed to about 5% conversion, the tubes were removed from the baths and the polymer separated from the monomer by precipitation with methanol. The polymer was washed in methanol for a period of a week, during which time the solution was changed every day. At the end of a week, the polymer was dried at 80 °C. under vacuum.

The chlorine-containing polymer samples were analyzed by the Parr bomb method. A weighed quantity of about 0.2 g. polymer was introduced into the bomb along with 15 g. Na_2O_2 and small amounts of KNO3 and sugar. These were mixed intimately. The bomb was exploded in the flame of a Bunsen burner and the contents washed into a beaker. The solution was acidified with nitric acid. 25 ml. 0.1 N AgNO3 was pipetted into the beaker and the solution was warmed to coagulate the AgCl formed. The excess AgNO3 was back-titrated with 0.1 N NH4CNS.

The nitrogen-containing polymers were analyzed by a modified Kjeldahl procedure,4 A

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 - ³ T. Alfrey, Jr., Merz, and H. E. Mark, J. Polymer Sci., 1, 37 (1946).
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weighed sample of about 0.3 gram was digested in the usual manner with sulfuric acid and selenium pellets. After the solution had become colorless, 50 ml. of distilled water and two drops of methyl red were added. The contents of the flask were made slightly alkaline by addition of 10 N NaOH

TABLE I
MONOMER AND POLYMER COMPOSITION

| C4mana | D: LL | rostvrene |
|-----------|----------|-----------|
| or viene. | - DICHEO | rostvrene |

| Experi- Mon | | mer, mole composition | | Polymer, mole composition, from Cl ₂ analysis (St/Dst) | |
|-------------|------------|-----------------------|------|---|--|
| nent No. St | Dst St/Dst | | | | |
| 1 | 0.0141 | 0.0650 | 0.22 | 0.39 0.39 | |
| 2 | 0.0712 | 0.0272 | 2.62 | 1.27 - 1.27 | |
| 3 | 0.0335 | 0.0364 | 0.93 | 0.86 0.87 | |
| 4 | 0.0218 | 0.0575 | 0.38 | 0.72 - 0.72 | |
| 5 | 0.0311 | 0.0311 | 1.00 | 0.95 - 0.96 | |
| 6 | 0.0843 | 0.0240 | 3.52 | 1.68 1.68 | |
| 7 | 0.0156 | 0.0624 | 0.25 | 0.93 - 0.93 | |
| 8 | 0.0368 | 0.0375 | 0.98 | , 1.20 1.20 | |
| 9 | 0.0588 | 0.0302 | 1.95 | 1.60 1.60 | |
| 10 | 0.0202 | 0.0747 | 0.27 | 0.99 0.99 | |
| 11 | 0.0415 | 0.0352 | 1.18 | 1.40 1.40 | |
| 12 | 0.0742 | 0.0308 | 2.41 | 1.99 1.99 | |

Styrene-Acrylonitrile

| Experiment No. St | Mo | nomer, mole compos | Polymer, mole composition, from N_2 analysis (St/Ac) | |
|-------------------|--------|--------------------|--|------------|
| | Ac | St/Ac | | |
| 25 | 0.0539 | 0.0691 | 0.78 | 1.21 1.21 |
| 26 | 0.0622 | 0.0386 | 1.61 | 1.58 1.58 |
| 27 | 0.0292 | 0.1328 | 0.22 | 0.92 0.92 |
| 28 | 0.0394 | 0.1232 | 0.32 | 1.02 1.03 |
| 29 | 0.0620 | 0.0187 | 3.32 | 2.44 2.45 |
| 30 | 0.0574 | 0.0296 | 1.94 | 1.89 1.90 |
| 31 | 0.0422 | 0.1300 | 0.32 | 1.07 1.07 |
| 32 | 0.0645 | 0.0321 | 2.01 | 2.01 2.02 |
| 33 | 0.0685 | 0.0240 | 2.86 | 2.34 2.35 |

Dichlorostyrene-Acrylonitrile

| Experi- | Mono | omer, mole composition | | Polymer, mole composition (Dst/Ac) | | |
|--------------|--------------|------------------------|-------------------------------|---------------------------------------|-----------|--|
| ment No. Dst | Dst Ac Dst/A | Dst/Ac | From Cl ₂ analysis | From N ₂ analysis | | |
| 13 | 0.0421 | 0.0421 | 1.00 | 0.87 0.88 | | |
| 14 | 0.0486 | 0.0114 | 4.26 | 1.26 1.25 | | |
| 15 | 0.0099 | 0.0825 | 0.12 | 0.31 0.31 | | |
| 16 | 0.0366 | 0.1408 | 0.26 | 0.56 0.56 | 0.56 0.57 | |
| . 17 | 0.0534 | . 0.1212 | 0.44 | 0.70 0.71 | 0.71 0.71 | |
| 18 | 0.0809 | 0.0190 | 4.26 | 1.27 1.27 | 1.27 1.27 | |
| 19 | 0.0198 | 0.0860 | 0.23 | 0.55 0.56 | | |
| 20 | 0.0306 | 0.0333 | 0.92 | 0.84 0.83 | | |
| 21 | 0.0393 | 0.0112 | 3.52 | 1.24 1.24 | | |
| 22 | 0.0646 | 0.0390 | 1.66 | 0.98 0.98 | 0.98 0.99 | |
| 23 | 0.0422 | 0.0980 | 0.43 | 0.75 .0.76 | 0.76 0.76 | |
| 24 | 0.0452 | 0.0173 | 2.62 | 1.14 1.15 | 1.15 1.15 | |

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(carbonate free). 1 N sulfuric acid was used to acidify the solution and 0.1 N NaOH (carbonate free) was used to titrate to the methyl-red end point. 30 ml. of an 18% formaldehyde solution, which had been titrated with 0.1 N NaOH to a phenolphthalein end point, was then added. The titration was continued to a faint yellow. 8 drops of phenolphthalein was added and the titration was continued to the phenolphthalein end point. The amount of reagent required to bring the solution from the methyl-red to the phenolphthalein end point is equivalent to the amount of nitrogen present.

RESULTS

The results of this investigation are recorded in Tables I, II, and III. Table I gives the results of the analyses; Table II gives the r values found experimentally; and Table III gives the difference of the energies of activation for the respective addition reactions.

In Table II:

Table II

r Values as Determined by Polarization

| | | Styrene-Dic | hlorostyrene | | |
|-------|-------|----------------|------------------|-----------------------|-----------------------|
| 41 | .5°C. | 65. | 0°C. | 86. | 5°C. |
| r_1 | r_2 | r_1 | r_2 | r_1 | r_2 |
| 0.11 | 0.17 | 0.26 | 0.04 | 0.37 | 0.03 |
| 0.22 | 0.19 | 0.33 | 0.05 | 0.41 | 0.03 |
| 0.24 | 0.34 | 0.37 | 0.13 | 0.42 | 0.08 |
| | | Styrene-A | crylonitrile | | |
| 41.5° | C. | 65. | 0°C. | 86.5 | °C. |
| r_1 | r_2 | r_1 | $oldsymbol{r}_2$ | r_1 | r_2 |
| 0.35 | 0.04 | 0.42 | -0.10 | 0.44 | -0.10 |
| 0.38 | 0.04 | 0.44 | 0.03 | 0.48 | 0.03 |
| 0.40 | 0.07 | 0.48 | 0.04 | 0.49 | 0.03 |
| | | Dichlorostyrer | ne-Acrylonitrile | ; | |
| 38.5 | °C. | 67.5 | °C. | 86 | 6.5°C. |
| r_1 | | r_1 | r_2 | <i>r</i> ₁ | r ₂ |
| 0.08 | 0.24 | 0.02 | 0.19 | 0.01 | 0.14 |
| 0.08 | 0.27 | 0.09 | 0.19 | 0.08 | 0.16 |
| 0.11 | 0.27 | 0.10 | 0.27 | 0.11 | 0.38 |

Table III Energy Differences

| Polymer | $E_{aa} - E_{ab},$ kcal. |
|---|--------------------------|
| Styrene-dichlorostyrene, r_1 | 4.1 ± 0.9 |
| Styrene-dichlorostyrene, r_2 | -8.3 ± 2.2 |
| Styrene-acrylonitrile, r_1 | 1.4 ± 0.2 |
| Styrene-acrylonitrile, r ₂ | -2.3 ± 0.5 |
| Dichlorostyrene-acrylonitrile, r_1 | -3.2 ± 0.1 |
| Dichlorostyrene-acrylonitrile, r ₂ | -1.1 ± 0.3 |

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$$\begin{split} r_1(\text{St-Dst}) &= k_{\text{StSt}}/k_{\text{StDst}}; & r_2 &= k_{\text{DstDst}}/k_{\text{DstSt}} \\ r_1(\text{St-Ac}) &= k_{\text{StSt}}/k_{\text{StAc}}; & r_2 &= k_{\text{AcAc}}/k_{\text{AcSt}} \\ r_1(\dot{\text{Dst-Ac}}) &= k_{\text{DstDst}}/k_{\text{DstAc}}; & r_2 &= k_{\text{AcAc}}/k_{\text{AcDst}} \end{split}$$

CONCLUSIONS

The rate constant ratios for acrylonitrile-styrene are virtually identical with those determined by Mayo, Lewis, and Hulse.¹ However, the values for the system styrene-dichlorostyrene are very different from those reported in the literature. No mention could be found of the dichlorostyrene-acrylonitrile values.

The values of the temperature dependence were of the order of magnitude expected except for the system styrene-dichlorostyrene, where values of 4.1 and -8.3 kcal. were observed. These values would indicate a high energy of activation for the addition of styrene—an unexpected result.

Synopsis

Copolymerization rate constant ratios have been determined as a function of temperature for the monomer pairs: styrene-acrylonitrile and dichlorostyrene-acrylonitrile. The temperature dependence, which represents the difference of the activation energies of the respective addition reactions, is of the magnitude expected, except for the styrene-dichlorostyrene system.

Résumé

Les rapports des constantes de vitesses de copolymérisation ont été étudiées en fonction de la température pour les paires de monomères: styrol-acrylonitrile et dichlorostyrol-acrylonitrile. La dépendance thermique, qui exprime la différence d'énergie d'activation des réactions d'additions respectives, est de l'ordre de grandeur prévu, sauf dans le cas de la paire styrol-dichlorostyrol.

Zusammenfassung

Das Verhältnis der Geschwindigkeitskonstanten der Mischpolymerization wird in Abhängigkeit von der Temperatur für die folgenden Monomerenpaare bestimmt: Styrol-Acrylonitril, Dichlorostyrol-Acrylonitril. Die Temperaturabhängigkeit, die die Differenz der Aktivierungenergien der respektive Additionsreaktionen beschreibt, ist für das System Styrol-Acrylonitril von der erwarteten Grössenordung.

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