

## COPOLYMERIZATIONS OF 2-HYDROXYETHYLMETHACRYLATE WITH VINYLPIRIDINES AND WITH N-SUBSTITUTED METHACRYLAMIDES

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**Abstract**—Studies were made of the copolymerizations of 2-hydroxyethylmethacrylate with 2-, 3- and 4-vinylpyridine, *N*-(*trans*-4'-nitro-4-stilbenyl)methacrylamide and *N*-(*trans*-4-stilbenyl)methacrylamide. Methods of Fineman–Ross, Joshi–Joshi, Tidwell–Mortimer and Tosi were employed to determine monomer reactivity ratios; the results for 2- and 4-vinylpyridine were compared with those calculated from the *Q*–*e* scheme. The monomer reactivity ratios for 2-hydroxyethylmethacrylate with vinylpyridines calculated by different methods showed good agreement. The monomer reactivity is briefly discussed.

### INTRODUCTION

Copolymers of 2-hydroxyethylmethacrylate with vinylpyridines were prepared to study catalytic properties of vinylpyridine polymers and to investigate their biological tolerance [1]. Similarly, copolymers of 2-hydroxyethylmethacrylate with *N*-(*trans*-4'-nitro-4-stilbenyl)methacrylamide and with *N*-(*trans*-4-stilbenyl)methacrylamide were prepared and the *trans*–*cis* photoisomerization of the stilbene moiety in the side chains of the copolymers was studied [2, 3]. Polymers, particularly gels based on 2-hydroxyethylmethacrylate are finding wide applications in surgery and medicine.

In the present work, a study was made of the copolymerization of 2-hydroxyethylmethacrylate (HEMA) with 2-, 3- and 4-vinylpyridines (2-, 3- and 4-VP), *N*-(*trans*-4'-nitro-4-stilbenyl)methacrylamide (NSMA) and *N*-(*trans*-4-stilbenyl)methacrylamide (SMA). The monomer reactivity ratios were calculated by several methods; values for 2- and 4-vinylpyridines were compared with those resulting from the *Q*–*e* scheme.

### EXPERIMENTAL

The copolymerizations of HEMA with 2-, 3- and 4-VP were carried out in bulk in ampoules at  $60^\circ \pm 0.1^\circ$  in the presence of *N,N'*-azobisisobutyronitrile. The air was expelled from the polymerization mixture by repeating several times the following cycle: freezing–evacuation–melting–purging with nitrogen. The polymers were precipitated in a mixture ether–petroleum ether; after two precipitations from methyl alcohol solution, they were dried at  $20^\circ$  and 1 mm Hg for 60 hr.

All copolymerizations of HEMA with SMA and NSMA were carried out in *N,N'*-dimethylformamide solvent at 0.5 M total monomer concentration in sealed ampoules with 0.2 mol % (related to the amount of monomers) of *N,N'*-azobisisobutyronitrile. The removal of air from the ampoules was achieved as above. The polymerization temperature was kept at  $60 \pm 0.1^\circ$ . The copolymer solution was precipitated in a 10-fold excess of anhydrous ether. Stilbene monomers were removed by dialysis through regenerated

cellulose membrane against a continuous flow of *N,N'*-dimethylformamide. The polymers were obtained by precipitation of dialysed solution in ether. Complete removal of stilbene monomers was thus achieved. The polymers were dried as above. Preparation and purification procedures for 2-VP, 3-VP, 4-VP and HEMA, SMA and NSMA will be published [1, 3].

Calculations of monomer reactivity ratios according to Fineman–Ross, Joshi–Joshi and Tidwell–Mortimer were carried out on the Tesla 200 digital computer at the computer centre of the Institute of Chemical Technology, Prague.

### RESULTS AND DISCUSSION

#### *Copolymerization of 2-hydroxyethylmethacrylate with 2-, 3- and 4-vinylpyridines*

For the composition of polymerization mixtures and composition of copolymers, see Table 1. The copolymers were analysed for nitrogen and the results were used to calculate the mole fractions of 2-, 3- and 4-VP in the copolymers.

#### *Copolymerization of 2-hydroxyethylmethacrylate with N-(trans-4-stilbenyl)methacrylamide and N-(trans-4'-nitro-4-stilbenyl)methacrylamide*

The compositions of polymerization mixtures and copolymers are summarized in Tables 2 and 3. The compositions of copolymers were determined by analysis as mentioned above and spectrometrically at  $\lambda_{\max}$  of the *trans*-isomer of copolymerized stilbene monomers [3]. Good agreement between the results for the two determinations demonstrated that  $\epsilon_{\text{trans}}^{\lambda_{\max}}$  of a stilbene unit in the copolymer is about the same as  $\epsilon_{\text{trans}}^{\lambda_{\max}}$  of its low-molecular analogue, *N*-(*trans*-4'-nitro-4-stilbenyl)isobutyroamide. Thus, it was also demonstrated that the monomer NSMA underwent copolymerization similarly as the other derivatives of the methacrylic acid without side reactions. The polymerization rate was found to decrease rapidly with increas-

Table 1. Copolymerization of 2-vinylpyridine (2-VP), 3-vinylpyridine (3-VP) and 4-vinylpyridine (4-VP) with 2-hydroxyethylmethacrylate (HEMA)

|      | Mole fraction<br>vinylpyridines<br>in monomer<br>( $f_{VP}$ ) | Mole fraction<br>vinylpyridines<br>in copolymer<br>( $F_{VP}$ ) |
|------|---|---|
| 2-VP | 0.1696  | 0.218   |
|      | 0.2409  | 0.273   |
|      | 0.2474  | 0.345   |
|      | 0.3568  | 0.407   |
|      | 0.4734  | 0.503   |
|      | 0.5512  | 0.557   |
|      | 0.6551  | 0.644   |
| 3-VP | 0.7616  | 0.704   |
|      | 0.2271  | 0.267   |
|      | 0.3443  | 0.369   |
|      | 0.4080  | 0.432   |
|      | 0.5224  | 0.528   |
|      | 0.6035  | 0.588   |
|      | 0.7493  | 0.721   |
| 4-VP | 0.2227  | 0.277   |
|      | 0.4459  | 0.500   |
|      | 0.5403  | 0.576   |
|      | 0.5460  | 0.586   |
|      | 0.6590  | 0.682   |
|      | 0.7365  | 0.730   |

N,N'-Azobisisobutyronitrile (0.05 mole %) as initiator, polymerization temperature  $60 \pm 0.1^\circ$ .

ing molar fraction of monomers SMA and NSMA. The decrease of reaction rate is a consequence of the inhibition by the stilbene moiety of the monomers SMA and NSMA. This inhibition is known in the case of aromatic nitrocompounds and aromatic hydrocarbons,

including stilbene [4]. The inhibition of the polymerization was demonstrated by adding *trans*-stilbene, *trans*-4-nitrostilbene, N-(*trans*-4-stilbenyl)isobutyroamide and N-(*trans*-4'-nitro-4-stilbenyl)isobutyroamide to the polymerization system instead of the monomers SMA and NSMA.

#### Determination of the monomer reactivity ratios

Determination of the monomer reactivity ratios from experimental data has been discussed [5, 6]. Application of a differential form of the copolymerization equation was considered and certain drawbacks associated with this method have been indicated. The differential form of the copolymerization equation, associated with the nonlinear least-square method used by Behnken [7] and Tidwell-Mortimer [5], was generally found the most suitable method for determining the monomer reactivity ratios. These methods are advantageous as compared with the method of Fineman-Ross [8] which is based on the differential copolymerization equation

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$$

and with the intersection method of Mayo-Lewis [9]. Besides the method of Tidwell-Mortimer, an approach by Joshi-Joshi [12] is acceptable and can be also used in connection with the intersection method based on the integrated copolymerization equation [13].

Several programs for digital computer [6, 10, 11] were worked out for calculating monomer reactivity ratios from the integrated form of the copolymerization equation.

The monomer reactivity ratios were calculated by the methods of Fineman-Ross, Tidwell-Mortimer, Joshi-Joshi (from the integrated copolymerization

Table 2. Copolymerization of N-(*trans*-4'-nitro-4-stilbenyl)methacrylamide (NSMA) with 2-hydroxyethylmethacrylate (HEMA)

| Mole fraction<br>NSMA<br>in monomer<br>( $f_{NSMA}$ ) | Conversion<br>(%) | Mole fraction<br>NSMA<br>in copolymer<br>( $F_{NSMA}^*$ ) | ( $F_{NSMA}^\dagger$ ) |
|---|-------------------|---|------------------------|
| 0.0505‡   | 33.0              | 0.025   | 0.026                  |
| 0.0504  | 7.5               | 0.021   | 0.021                  |
| 0.0996‡   | 29.6              | 0.043   | —                      |
| 0.1971  | 4.2               | 0.136   | 0.138                  |
| 0.3019  | 5.1               | 0.233   | 0.228                  |
| 0.5000  | 1.8               | 0.393   | 0.391                  |
| 0.6700  | 2.3               | 0.562   | —                      |
| 0.8021  | 2.8               | 0.713   | —                      |
| 0.9063  | 2.4               | 0.855   | —                      |
| 1.0000  |                   | Trace amount of the polymer                               |                        |

\* Based on elemental analysis (N).

† Based on spectrometrical measurements in  $CH_3OH$ .

‡ Data omitted in calculating monomer reactivity ratios from a differential form of the copolymerization equation because of high conversion, concentration of monomers 0.5 M (in N,N'-dimethylformamide), 0.2 mole % N,N'-azobisisobutyronitrile (related to monomers), polymerization temperature  $60 \pm 0.1^\circ$ .

Table 3. Copolymerization of N-(*trans*-4-stilbenyl)methacrylamide (SMA) with 2-hydroxyethylmethacrylate (HEMA)

| Mole fraction SMA<br>in monomer<br>( $f_{\text{SMA}}$ ) | Conversion<br>(%) | Mole fraction SMA<br>in copolymer<br>( $F_{\text{SMA}}^*$ ) |
|---|-------------------|---|
| 0.0500  | 8.5               | 0.031   |
| 0.0600  | 7.2               | 0.031   |
| 0.1000  | 8.3               | 0.062   |
| 0.2000  | 5.1               | 0.122   |
| 0.3000  | 4.7               | 0.192   |
| 0.5000  | 2.1               | 0.384   |
| 0.6000  | 8.4               | 0.488   |
| 0.8000  | 6.9               | 0.728   |
| 1.0000  |                   |   |

Trace amount of the polymer

\* For reaction conditions and notes, see Table 2.

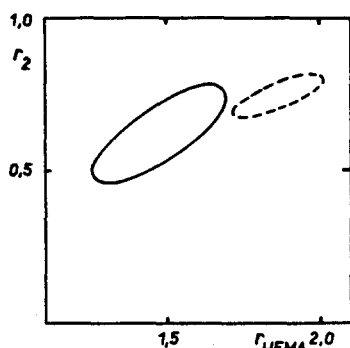


Fig. 1. The 95 per cent joint confidence limits for the systems: (----) SMA-HEMA and (—) NSMA-HEMA.

equation [13]) and Tosi [14] (Table 4). Figures 1 and 2 show the 95 per cent joint confidence limits for the values of  $r_{\text{HEMA}}$  and  $r_2$  for the nonlinear least squares method according to Tidwell-Mortimer [5]. To varying extents, there was agreement between results of these methods for individual monomer pairs. Good agreement may be observed for monomer pairs with vinylpyridines. For N-substituted methacrylamides, there is a larger deviation owing to poorer experimental data. A rather large deviation has been found for N-(*trans*-4'-nitro-4-stilbenyl)methacrylamide. In particular, the second pair of monomer reactivity ratios

determined by the method of Fineman-Ross differs considerably from the other methods. The methods of Tidwell-Mortimer and Joshi-Joshi for calculating the monomer reactivity ratios yield almost identical results for all vinylpyridines. This was also verified generally by model calculations of monomer reactivity ratios for data showing different spread, and various monomer reactivity ratios simulated by a computer [13]. One should also consider that the calculation according to Joshi-Joshi is much simpler than the nonlinear regression of Tidwell and Mortimer which

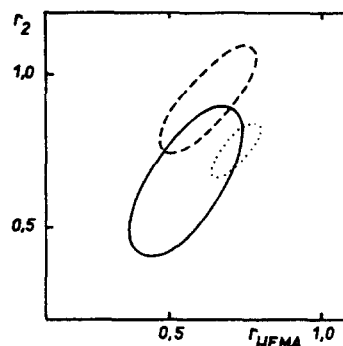


Fig. 2. The 95 per cent joint confidence limits for the systems: (—) 2-VP-HEMA, (.....) 3-VP-HEMA and (----) 4-VP-HEMA.

Table 4. Monomer reactivity ratios of 2-hydroxyethylmethacrylate (HEMA) with N-(*trans*-4-stilbenyl)methacrylamide (SMA), N-(*trans*-4'-nitro-4-stilbenyl)methacrylamide (NSMA) and 2-, 3- and 4-vinylpyridine (2-, 3-, 4-VP)

| Monomer (2) | Fineman-Ross    |                   | Joshi-Joshi     |                   | Tidwell-Mortimer |                   | Tosi  |                   |
|-------------|-----------------|-------------------|-----------------|-------------------|------------------|-------------------|-------|-------------------|
|             | $r_2$           | $r_{\text{HEMA}}$ | $r_2$           | $r_{\text{HEMA}}$ | $r_2$            | $r_{\text{HEMA}}$ | $r_2$ | $r_{\text{HEMA}}$ |
| SMA         | $0.50 \pm 0.47$ | $1.73 \pm 0.09$   | $0.72 \pm 0.03$ | $1.82 \pm 0.11$   | 0.74             | 1.86              | 0.71  | 1.51              |
|             | $0.73 \pm 0.02$ | $1.83 \pm 0.06$   |                 |                   |                  |                   |       |                   |
|             | $0.62 \pm 0.03$ | $1.72 \pm 0.15$   | $0.84 \pm 0.14$ | $1.94 \pm 0.32$   | 0.59             | 1.46              | 0.64  | 2.15              |
| NSMA        | $1.65 \pm 0.41$ | $2.52 \pm 0.11$   |                 |                   |                  |                   |       |                   |
|             | $0.57 \pm 0.04$ | $0.50 \pm 0.07$   | $0.65 \pm 0.04$ | $0.56 \pm 0.08$   | 0.65             | 0.56              | —     | —                 |
| 2-VP        | $0.69 \pm 0.21$ | $0.58 \pm 0.06$   |                 |                   |                  |                   |       |                   |
|             | $0.74 \pm 0.01$ | $0.71 \pm 0.02$   | $0.75 \pm 0.01$ | $0.72 \pm 0.01$   | 0.75             | 0.72              | —     | —                 |
| 3-VP        | $0.78 \pm 0.03$ | $0.74 \pm 0.01$   |                 |                   |                  |                   |       |                   |
|             | $0.83 \pm 0.04$ | $0.54 \pm 0.07$   | $0.89 \pm 0.04$ | $0.61 \pm 0.03$   | 0.92             | 0.63              | —     | —                 |
| 4-VP        | $0.95 \pm 0.04$ | $0.66 \pm 0.01$   |                 |                   |                  |                   |       |                   |

must be associated with the use of a digital computer.

For the copolymerization pairs 2-VP-HEMA and 4-VP-HEMA, the monomer reactivity ratios were calculated from the  $Q$ - $e$  scheme. The parameters  $Q$  and  $e$  were taken from the literature [15, 16]. Reasonable agreement was observed when comparing the experimentally found monomer reactivity ratios with the calculated values. It should be noted, however, that there are differences between values for  $Q$  and  $e$  calculated for 2- and 4-vinylpyridine on the basis of different comonomers.

The experimentally found monomer reactivity ratios (Table 4) conform to the Lewis-Mayo copolymerization Eqn. (1). In no case, was there evidence of a penultimate group effect.

Nevertheless, owing to scatter in the determination of monomer reactivity ratios, it has not been possible to decide whether copolymerization proceeds by the first-order Markov process or not. A similar observation was also made for other comonomers with vinylpyridines, i.e. alkylacrylates and alkylmethacrylates [16, 17]. The first-order Markov process could be confirmed by sequence structure analysis of copolymers.

The tendency for alteration with HEMA increases in the sequence: NSMA, SMA, 4-VP, 3-VP and 2-VP. The reactivities of 2-, 3-, 4-vinylpyridines do not differ greatly for copolymerization with 2-hydroxyethylmethacrylate. The resonance stabilization of 2-, 3- and 4-vinylpyridines is comparable with that of 2-hydroxyethylmethacrylate; a higher reactivity of radicals of vinylpyridine with its monomer may result from a different polarity as compared to 2-hydroxyethylmethacrylate as can be approximately demonstrated by values  $Q$  and  $e$  (the average  $Q$  and  $e$  values are as follows: for 2-VP 1.0–1.2 and  $-0.4$ – $0.6$ , respectively, for 3-VP and 4-VP 0.8–1.0 and  $-0.2$ – $0.4$ , respectively, and for 2-hydroxyethylmethacrylate 0.8 and 0.2, respectively).

#### CONCLUSION

The monomer reactivity ratios of 2-hydroxyethylmethacrylate with 2-, 3- and 4-vinylpyridines, *N*-(*trans*-

4-stilbenyl)methacrylamide and *N*-(*trans*-4'-nitro-4-stilbenyl)methacrylamide were determined by various methods. Owing to limited accuracy of experimental data for copolymer compositions, large scatter in monomer reactivity ratios has been observed in some cases. Reasonable agreement existed between experimentally found monomer reactivity ratios and those calculated from the  $Q$ - $e$  scheme. Sequence structure analysis of copolymers could reveal whether or not a penultimate effect exists.

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**Résumé**—On a étudié les copolymérisations du hydroxy-2-éthylméthacrylate avec les vinyl-2-, 3- et 4-pyridine, le *N*-(*trans*-nitro-4'-stilbényl-4) méthacrylamide et le *N*-(*trans*-stilbényl-4) méthacrylamide. On a utilisé les méthodes de Finemann-Ross, Joshi-Joshi, Tidwell-Mortimer et Tosi pour déterminer les rapports de réactivité des monomères; les résultats obtenus avec les vinyl-2 et -4 pyridines étaient comparés à ceux calculés à partir d'un schéma  $Q$ - $e$ . Les rapport de réactivité du hydroxy 2-éthylméthacrylate et des vinylpyridines calculés par différentes méthodes sont en bon accord. On discute brièvement de la réactivité du monomère.

**Zusammenfassung**—Untersucht wurden die Copolymerisationen von 2-Hydroxyäthylmethacrylat mit 2-, 3- und 4-Vinylpyridin, *N*-(*trans*-4'-Nitro-4-stilbenyl)-methacrylamid und *N*-(*trans*-4-Stilbenyl)-methacrylamid. Dabei wurden die Verfahren von Finemann-Ross, Joshi-Joshi, Tidwell-Mortimer und Tosi zur Bestimmung der Reaktivitätsverhältnisse der Monomeren benutzt. Die Ergebnisse für 2- und 4-Vinylpyridin wurden mit denen verglichen, die aus dem  $Q$ - $e$ -Schema berechnet wurden. Die Reaktivitätsverhältnisse des Monomeren 2-Hydroxyäthylmethacrylat mit den Vinylpyridinen, die nach verschiedenen Methoden berechnet wurden, zeigen gute Übereinstimmung. Die Monomerenreaktivität wird kurz diskutiert.