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Effect of Temperature on the Monomer Reactivity Ratios of 2-Hydroxypropyl Methacrylate with Ethyl- and Butyl-Acrylates

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(Received 22 May 1981)

SUMMARY:

2-Hydroxypropyl methacrylate has been copolymerized with ethyl acrylate and n-butyl acrylate in bulk at temperatures between 60 and 100°C using benzoyl peroxide as initiator. The compositions of copolymers have been analyzed by hydroxyl determination; the reactivity ratios have been calculated by Kelen-Tüdös method. Arrhenius parameters have been derived. The intrinsic viscosities and the thermal behaviours of the copolymers were also studied.

ZUSAMMENFASSUNG:

2-Hydroxypropylmethacrylat wurde mit Ethylacrylat und n-Butylacrylat in Masse bei Temperaturen zwischen 60 und 100°C copolymerisiert unter Verwendung von Benzoylperoxid als Initiator. Die Zusammensetzung der Copolymeren wurde durch Hydroxylgruppenbestimmung analysiert; die Copolymerisationsparameter wurden nach der Kelen-Tüdös-Methode berechnet. Die Arrheniusparameter wurden abgeleitet, und die Grenzviskositäten und das thermische Verhalten der Copolymeren wurden ebenfalls untersucht.

Introduction

Hydrophilic gels based on hydroxy acrylates have been employed in a number of prosthetic applications as contact lenses, pressure sensitive adhesives and as implants for localized slow release of drugs¹. Copolymerization of 2-hydroxypropyl methacrylate (HPMA) with alkyl acrylates was reported earlier². The effects of temperature on copolymerization have been studied for a large number of systems^{3–14}. However, there have been no

reports on the temperature dependence of reactivity ratios for HPMA-alkyl acrylate copolymers.

In the present investigation we report the effect of temperature on reactivity ratios of HPMA-ethylacrylate (EA) and HPMA-n-butylacrylate (BA) copolymers; the effect of hydroxyl content in the copolymer on viscosity, solubility and thermal properties of copolymers was also studied.

Experimental

Materials

HPMA (BDH) was obtained as middle cuts in reduced pressure distillation. The monomers ethyl acrylate (EA) and n-butyl acrylate (BA) were purified by standard methods; they were distilled over 4 Å molecular sieves. Benzoyl peroxide (BDH) was recrystallized from methanol.

Predetermined amounts of HPMA and alkyl acrylates were charged in a reaction tube. The tubes were sealed under vacuum by four freeze-thaw cycles. Polymerization was done in a constant temperature bath at temperatures between 60–100°C. After requisite time, the contents of the tubes were poured into n-heptane. The purified copolymers were dried at 50°C under vacuum to constant weight. The compositions of copolymers were determined from hydroxyl content determination by acetylation with a mixture of acetic anhydride and pyridine (1:3 v/v)².

The intrinsic viscosities were determined in dry dimethylformamide (DMF) in an Ubbelohde viscometer at $30 \pm 0.05^\circ\text{C}$. Thermogravimetric analysis (TGA) was carried out with Stanton Redcroft TG-750 thermobalance in nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$.

Results and Discussion

The reactivity ratios have been calculated from copolymer compositions using Kelen-Tüdös method¹⁵. The results are summarized in Tab. 1.

The higher r_1 value in HPMA-EA compared to HPMA-BA indicates the reactivity of alkyl acrylates in copolymerization may be influenced by the polar nature of the alkyl group. In BA, the greater electron releasing effect of the butyl group renders carbonyl less polar thereby decreasing the conjugation between carbonyl and vinyl as compared to EA. This will increase the rate constant for the steps involving addition of BA monomer with poly-HPMA radical i.e. r_1 decreases.

The values of r_1 , r_2 for both systems tend to increase with increasing copolymerization temperature. The increase in r_1 value is more than that of r_2

Effect of Temperature on the Monomer Reactivity

Tab. 1. Variation of reactivity ratios with temperature.

| Monomer reactivity ratio | Polymerization temperature (°C) | | | | |
|--------------------------|---------------------------------|--------|--------|--------|--------|
| | 60 | 70 | 80 | 90 | 100 |
| r ₁ (HPMA) | 13.038 | 13.942 | 15.840 | 17.319 | 19.159 |
| r ₂ (EA) | 0.223 | 0.270 | 0.310 | 0.359 | 0.431 |
| r ₁ (HPMA) | 5.170 | 6.549 | 7.543 | 8.316 | 9.636 |
| r ₂ (BA) | 0.238 | 0.323 | 0.311 | 0.361 | 0.421 |

for HPMA-BA, which suggests that HPMA is prone to self-propagation at higher temperatures. In other words, HPMA-BA copolymer consists of larger blocks of HPMA interspersed with BA units. For HPMA-EA system, the reactivity ratios do not change significantly with respect to the temperature. Further increase in reaction temperature increases r_1 value more for HPMA-BA than for HPMA-EA. This is probably due to the greater diffusivity of EA than BA to react with poly-HPMA radical and thus revealing the presence of steric factors even at higher reaction temperatures.

The Arrhenius relationship between reactivity ratios and temperature may be expressed as

$$\ln r_1 = \ln \frac{A_{11}}{A_{12}} - \frac{E_{11} - E_{12}}{RT}$$

where A is the frequency factor and E is an apparent energy of activation. The subscripts '11' and '12' refer to self-propagation and cross-propagation of the growing radical $\sim M_1^*$, respectively. In terms of transition state theory the relationship becomes

$$\ln r_1 = \frac{S_{11} - S_{12}}{R} - \frac{H_{11} - H_{12}}{RT}$$

Fig. 1 shows the Arrhenius parameters given in Tab. 2. In both systems the difference in activation energy favours cross propagation of poly-HPMA radical whereas preexponential factors A_{11}/A_{12} favour the self propagation. For the EA and BA radicals also the activation energies and frequency factors (A_{22}/A_{21}) favour cross propagation and self addition, respectively.

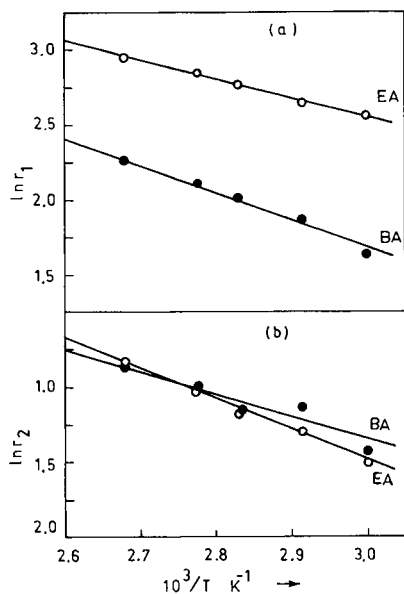


Fig. 1. Arrhenius plots for the reactivity ratios; a: r_1 (HPMA); b: r_2 (EA or BA).

Tab. 2. Arrhenius parameters for reactivity ratios.

| Monomer | Differences in energies of activation (kJ mol ⁻¹) | Ratio of frequency factors | Differences in entropies of activation (JK ⁻¹ mol ⁻¹) |
|------------------------|---|----------------------------|--|
| HPMA (M ₁) | 10.15 ± 0.05 | 501.35 ± 8.75 | 51.70 ± 0.15 |
| EA (M ₂) | 16.61 ± 0.01 | 1.95 ± 0.00 | 37.38 ± 0.02 |
| HPMA (M ₁) | 15.36 ± 0.02 | 1389 ± 115 | 60.08 ± 0.07 |
| BA (M ₂) | 12.98 ± 0.02 | 1.44 ± 0.05 | 27.51 ± 0.08 |

Thus $E_{i1} - E_{i2}$ values favour the cross propagation in the order BA > EA, whereas the frequency factors (A_{i1}/A_{i2}) indicate the following order for cross propagation: EA > BA. The r_1 values, however, show cross propagation in the order BA > EA. It may be concluded that the relative reactivities of alkyl acrylates toward HPMA radical depend on the polarity of monomers, on the steric factors and on the resonance stabilization of radicals.

Characterization and Properties

In order to compare the properties of different polymers, copolymerizations were carried out making use of reactivity ratios data to get desired compositions of monomers in the copolymer feed (Tab. 3).

Tab. 3. Copolymerization of HPMA (M_1) and alkyl acrylates (M_2) in bulk.

| No. | M_1 , mole fraction of monomer | Conversion (%) | m_1 mole fraction of M_1 in copolymer | $[\eta]$ (dl/g) |
|---------|--|-------------------|--|--------------------|
| HPMA-EA | | | | |
| 1 | 0.056 | 5.5 | 0.233 | 3.75 |
| 2 | 0.118 | 5.8 | 0.445 | 3.65 |
| 3 | 0.237 | 9.1 | 0.668 | 2.55 |
| HPMA-BA | | | | |
| 4 | 0.048 | 10.1 | 0.145 | 1.0 |
| 5 | 0.128 | 13.0 | 0.342 | 2.22 |
| 6 | 0.351 | 11.5 | 0.632 | 2.36 |

Copolymers with $m_1 > 0.8$ were not soluble in DMF, which may be due to strong intermolecular interactions arising from hydroxyl groups or partial crosslinking.

The intrinsic viscosities of HPMA-EA decreased with the increase of HPMA proportion in the copolymers. However, in HPMA-BA the reverse trend was observed. It may be assumed that the steric interactions between BA units at the radical chain end is high with the penultimate HPMA unit leading to slower segmental diffusion due to hindered rotation about polymer chain axis, i. e. the cross-termination is reduced due to bulky groups. On the other hand, in HPMA-EA copolymers, the effective interactions of hydroxyl groups of HPMA, present penultimate to the EA radical chain end makes the rotation of propagating ends relatively easy thereby facilitating the cross-termination of radicals.

The heat stabilities of the copolymers were assessed by TGA in nitrogen. The thermograms of copolymers indicate a one stage weight loss (Fig. 2 and 3). The increase in HPMA proportion of copolymers decreases the stability.

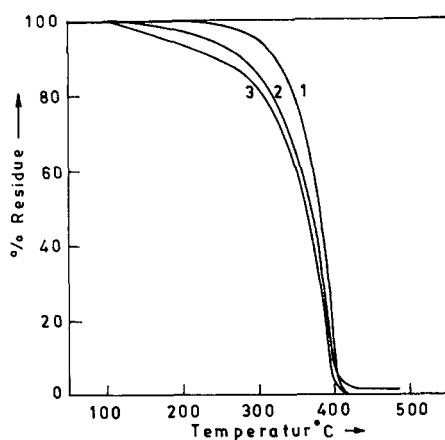


Fig. 2. Thermogravimetric analysis; 1: HPMA (0.342) – BA (0.658) mole fraction; 2: HPMA (0.632) – BA (0.368) mole fraction; 3: HPMA (0.810) – BA (0.190) mole fraction.

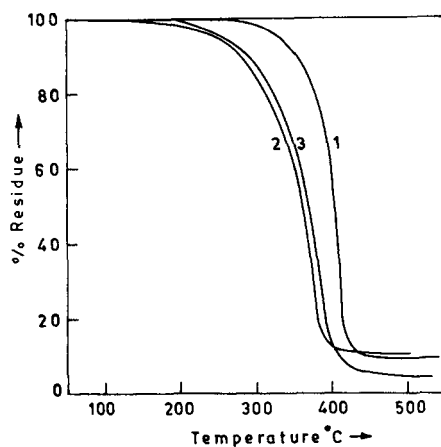


Fig. 3. Thermogravimetric analysis; 1: HPMA (0.233) – EA (0.767) mole fraction; 2: HPMA (0.445) – EA (0.555) mole fraction; 3: HPMA (0.668) – EA (0.332) mole fraction.

The relative thermal stability of various copolymers was also assessed from these thermograms considering the decomposition temperature at a

Tab. 4. Thermogravimetric analysis of HPMA-alkyl acrylate copolymers.

| No. | Polymer ^a | m _i (mol-%) | IDT (°C) ^b | DT at different weight losses (°C) | | | | D _{max} (°C) ^c | IPDT (°C) ^d |
|-----|----------------------|---------------------------|--------------------------|------------------------------------|-----|-----|-----|---------------------------------------|---------------------------|
| | | | | 10% | 20% | 40% | 60% | 80% | |
| 1 | E ₁ | 0.233 | 243 | 359 | 379 | 399 | 409 | 418 | 397 |
| 2 | E ₂ | 0.445 | 181 | 286 | 313 | 349 | 368 | 381 | 375 |
| 3 | E ₃ | 0.668 | 124 | 288 | 324 | 361 | 379 | 392 | 380 |
| 4 | B ₁ | 0.342 | 202 | 323 | 348 | 374 | 384 | 391 | 380 |
| 5 | B ₂ | 0.632 | 106 | 280 | 321 | 357 | 377 | 389 | 378 |
| 6 | B ₃ | 0.810 | 97 | 243 | 311 | 357 | 374 | 390 | 375 |

^a Polymers: E-Hydroxypropyl methacrylate-ethyl acrylate copolymer; B-Hydroxypropyl methacrylate-butyl acrylate copolymer.

^b IDT — initial decomposition temperature.

^c D_{max} — maximum decomposition temperature.

^d IPDT — integral procedural decomposition temperature.

particular weight loss (10–80%) (Tab. 4). The stabilities of HPMA-EA copolymers exceed those for HPMA-BA copolymers; the difference becomes less as the hydroxyl content increases in the copolymer. The stability is in accordance with the size of the alkyl substituent. The integral procedural decomposition temperatures (IPDT) indicate greater thermal stability for HPMA-EA copolymers than for HPMA-BA copolymers.

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