Polymer Bulletin 6, 1-6 (1981)

Polymer Bulletin

Effect of Temperature on the Monomer Reactivity Ratios of 2-Hydroxypropyl Methacrylate with Methyl Acrylate and Methyl Methacrylate

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Summary

2-Hydroxypropyl methacrylate (2-HPMA) has been copolymerized with methyl acrylate (MA) and methyl methacrylate (MMA) in bulk at temperatures between 60 and 100°C using benzoyl peroxide as initiator. The compositions of copolymers have been determined by hydroxyl content; the reactivity ratios have been calculated by Kelen Tüdös method. The intrinsic viscosities and thermal behaviour of the copolymers were also studied.

Introduction

The polymers containing hydroxyl group in the side chain have become increasingly important in recent years for applications as coatings and pressure sensitivity adhesives (YOCUM and NYQUIST, 1973). Copolymers of 2-HPMA with several vinyl monomers have been reported (BABU et al, 1977); (BAJAJ et al, 1979).

This article, therefore, deals with the effect of temperature on reactivity ratios of 2-HPMA-MA and 2-HPMA-MMA copolymer systems. The effect of hydroxyl content on viscosity and thermal behaviour of copolymers was studied.

Experimental

The monomers MA (BDH) and MMA (SISCO) were freed from the inhibitor by washing with 10% sodium hydroxide and then with water and finally dried over magnesium sulfate. The monomers MA, MMA and 2-HPMA (BDH) were purified by distillation under reduced pressure.

Benzoyl peroxide (BDH) was recrystallized from methanol.

0170-0839/81/0006/0001/$01.20

Polymerization was carried out as described earlier (BABU et al,1981). The compositions of copolymers were determined from hydroxyl content estimation by acetylation with a mixture of acetic anhydride and pyridine (1/3 v:v) (BABU et al, 1977).

The intrinsic viscosities were determined in dry dimethylformamide (DMF) in an Ubbelohde viscometer at 30 ± 0.05°C.

Thermogravimetric analyses (TGA) of polymers were carried out using Stanton Redfort TG-750 thermobalance in nitrogen at a heating rate of 10°C/min.

Results and Discussion

The radical copolymerization of 2-HPMA with MA and MMA was carried out in the temperature range 60-100°C. Table 1 summarizes the values of monomer reactivity ratios obtained by Kelen-Tüdös method (KELEN and TÜDÖS, 1975).

Table 1. Variation of reactivity ratios with temperature

Monomer reactivity ratio	Polymerization temperature °C				
	60	70	80	90	100
r_1 (2-HPMA)	7.369	9.961	16.600	18.874	20.000
r_2 (MA)	0.015	0.049	0.100	0.263	0.244
r_1 (2-HPMA)	1.055	1.320	1.420	1.561	1.700
r_2 (MMA)	0.403	0.526	0.502	0.536	0.572

A perusal of the reactivity ratio data shows rather high values for r_1 and low values for r_2 (Table 1). This reveals that MA/MMA monomer is less reactive than 2-HPMA towards the poly(2-HPMA) radical. Further the increase in temperature increases both r_1 and r_2 values. This suggests that the tendency to self propagation predominates at higher reaction temperatures irrespective of the value of the reactivity ratios.

Characterization and Properties

In order to compare properties of different polymers, copolymerizations were carried out by making use of reactivity ratio data to get desired compositions of monomers in the copolymer feed (Table 2).

Table 2. Copolymerization of 2-HPMA (M_1) and alkyl acrylates (M_2) in bulk at 70°C

Sr. No.	M_1 mole fraction of polymer	Conversion %	m_1 mole fraction in copolymer	$[\eta]$ dl/gm
		2-HPMA - MA		
1	0.019	7.5	0.248	4.75
2	0.041	11.4	0.401	3.37
3	0.137	9.1	0.665	2.95
		2-HPMA - MMA		
4	0.119	8.6	0.194	0.52
5	0.290	9.1	0.402	1.08
6	0.577	10.2	0.669	1.48

The intrinsic viscosities of 2-HPMA-MA copolymers decrease with increase in 2-HPMA proportion while in the case of 2-HPMA-MMA copolymers the intrinsic viscosities increase . The cross termination of growing radicals may be favoured in 2-HPMA-MA copolymers as MA proportion increases in copolymers which may be due to the small size of ester group. On the other hand in 2-HPMA-MMA copolymers the cross termination reactions are progressively decreased with increase of 2-HPMA content in the copolymers which may be attributed to the size of active growing radical ends. The decrease in cross termination reactions would influence the increase in the kinetic chain length and consequently viscosity.

The heat stabilities of copolymers were assessed by TGA in nitrogen atmosphere. The thermograms of poly MA, poly MMA, poly 2-HPMA and the copolymers indicate a one stage weight loss under the experimental conditions (Figs. 1 and 2).

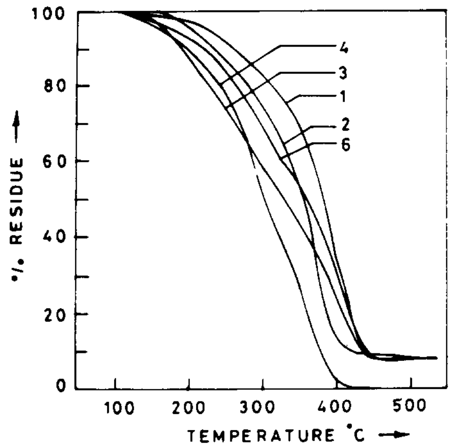

Fig. 1 Thermogravimetric analysis

1) Poly 2-HPMA
2) Poly MMA
3) 2-HPMA (0.194) - MMA (0.806)
4) 2-HPMA (0.402) - MMA (0.598)
6) 2-HPMA (0.818) - MMA (0.182)

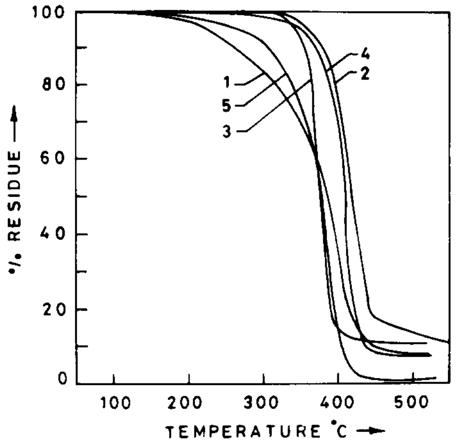

Fig. 2 Thermogravimetric analysis

1) Poly 2-HPMA
2) Poly MA
3) 2-HPMA (0.248) - MA (0.752)
4) 2-HPMA (0.401) - MA (0.599)
5) 2-HPMA (0.665) - MA (0.335)

The increase in the 2-HPMA proportion in 2-HPMA MA copolymers resulted in a decrease in thermal stability as noticed from the decomposition temperature at various weight losses (Table 3). The integral procedural decomposition temperature (IPDT) values of M_1, M_3 and M_4 do not change significantly.

Table 3. Thermal gravimetric analysis of 2-HPMA-alkyl acrylate copolymers

Polymer[a]	m_1 mole %	DT at different weight losses °C					D_{max} °C[b]	IPDT °C[c]
		10%	20%	40%	60%	80%		
M_0	-	381	395	412	425	441	415	423
M_1	0.248	355	364	373	380	386	373	375
M_2	0.401	369	385	403	411	422	420	405
M_3	0.665	303	337	369	382	393	375	370
M_4	0.816	312	336	362	374	390	375	362
MM_0	-	233	280	339	363	386	380	336
MM_1	0.194	194	222	296	364	402	360	314
MM_2	0.402	204	244	287	326	353	325	292
MM_3	0.669	226	250	286	329	371	-	335
MM_4	0.818	224	260	331	381	416	375	342
H	1.00	257	321	369	393	418	366	387

[a] Polymers - M_0 - Methyl acrylate; M - 2-Hydroxypropyl methacrylate - methyl acrylate copolymer; MM_0 - Methyl methacrylate; MM - 2-Hydroxypropyl methacrylate - methyl methacrylate copolymer; H - 2-Hydroxypropyl methacrylate

[b] D_{max} - maximum decomposition temperature

[c] IPDT - integral procedural decomposition temperature

In 2-HPMA-MMA copolymers, an increase in 2-HPMA content showed an increase in stability. MMA and 2-HPMA possessed quaternary carbon atoms in the repeating unit and hence the tendency to form a tertiary radical by random scission is expected to take place. The increased stability of 2-HPMA-MMA copolymers however, may be due to hydroxyl cross-linking.

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Received June 9, 1981
Revised September 25, 1981
Accepted October 15, 1981