

Statistical group transfer copolymerization of acrylates with methacrylates

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Statistical group transfer copolymerization (GTP) of acrylates with methacrylates have been performed for four binary systems using 1-methoxy-2-methyl-1-trimethylsilyloxypropene (initiator) and tetrabutylammonium bibenzoate (catalyst) in tetrahydrofuran solution. The copolymer compositions were determined by ^1H n.m.r. spectroscopy and the results evaluated by the extended Kelen–Tüdös method. The monomer pairs concerned are (1) ethyl acrylate (EA) and methyl methacrylate (MMA), (2) methyl acrylate (MA) and ethyl methacrylate (EMA), (3) MA and butyl methacrylate (BMA) and (4) MA and iso butyl methacrylate (i-BMA). The reactivity ratios were found to be $\gamma_{\text{EA}} = 14.15$, $\gamma_{\text{MMA}} = 0.01$, $\gamma_{\text{MA}} = 14.41$, $\gamma_{\text{EMA}} = 0.01$, $\gamma_{\text{MA}} = 13.96$, $\gamma_{\text{BMA}} = 0.23$, $\gamma_{\text{MA}} = 8.66$ and $\gamma_{\text{iBMA}} = 0.08$, respectively. Statistical anionic copolymerizations were also carried out for two monomer pairs to compare with the results for GTP. The reactivity ratios are $\gamma_{\text{EA}} = 9.67$, $\gamma_{\text{MMA}} = 0.11$, $\gamma_{\text{MA}} = 3.51$ and $\gamma_{\text{EMA}} = 0.20$. It was found that acrylate is much more reactive than methacrylate; the reactivity ratios are quite different from unity and show a high similarity in GTP and anionic polymerization.
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INTRODUCTION

Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. Acrylic formulations based on alkyl acrylate copolymers are of practical interest in the preparation of coatings, membranes, adhesives and sealants, because of the wide range of glass transition temperatures covered by an appropriate selection of the copolymer system, as well as by their excellent chemical and optical properties. Group transfer polymerization (GTP) is useful for the preparation of statistical and block copolymers of acrylic monomers. The monomer reactivity ratios for GTP have been determined for a variety of methacrylates^{1–4}. It is well known that acrylates polymerize more rapidly than methacrylates in GTP, but little quantitative information about the monomer reactivity ratios for acrylate with methacrylate is available.

In our recent publications, we reported the monomer reactivity ratios of acrylonitrile with methacrylates or acrylates⁵ and of methyl methacrylate (MMA) with methyl acrylate (MA), of MMA with butyl acrylate (BA)⁶ by GTP. As a continuation, we have chosen four binary systems of acrylates with methacrylates for examination.

EXPERIMENTAL

Materials

1-Methoxy-2-methyl-1-trimethylsilyloxypropene (MTS)

was prepared according to the literature⁷, as was tetrabutylammonium bibenzoate (TBABB)⁸. Inhibitor-free acrylic monomers of high purity were stirred with calcium hydride for two days and freshly distilled under reduced pressure before use. Tetrahydrofuran (THF) was purified by refluxing over a fresh sodium benzophenone complex (a deep purple colour indicating a moisture free solvent). Anionic polymerization initiator n-butyl-lithium, as a 15.03% hexane solution, was obtained from Aldrich.

Copolymerization procedure

The monomer mixture (~ 0.02 mol), the initiator MTS (0.005–0.010 ml) and THF as solvent were mixed under an atmosphere of N_2 . The catalyst TBABB was then added as a solution (0.2 M) in acetonitrile. The mixture immediately warmed; the temperature rose 10–20°C, depending on the amount of MTS. After stirring for 5 min, a few drops of methanol were added to quench the reaction. The copolymer was then poured into petroleum ether (b.p. 30–60°C) and purified by several precipitations from THF solution into petroleum ether, and was then dried *in vacuo* at 40°C overnight. The anionic copolymerization was carried out in THF solution, initiated by n-butyl-lithium at –40°C under a N_2 atmosphere, following the same purification process. Pure copolymers were confirmed by n.m.r., i.r. spectroscopy and g.p.c.; ^1H n.m.r. analysis showed no residual monomer and no trimethylsilyl group.

Measurements

The ^1H n.m.r. spectra were recorded on a Varian Unity Plus-500 spectrometer for 5% (w/v) polymer solution in CDCl_3 at 298 K, and tetramethylsilane was

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Table 1 Statistical group transfer copolymerization of acrylates (M_1) with methacrylates (M_2)

No.	M_1 - M_2	M_1/M_2	$M_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D	Yield (%)
1	EA/MMA	1.18	5.37	6.50	1.21	19
2	EA/MMA	0.33	6.78	7.93	1.17	24
3	MA/EMA	1.69	4.57	5.71	1.25	16
4	MA/EMA	0.46	5.70	6.89	1.21	18
5	MA/BMA	2.13	5.70	7.51	1.32	21
6	MA/BMA	0.58	7.18	9.19	1.28	24
7	MA/iBMA	1.41	4.22	7.51	1.78	26
8	MA/iBMA	0.83	3.89	6.26	1.61	22

Table 2 Data for group transfer copolymerization of EA with MMA including the extended Kelen-Tüdös parameters

EA (mol)	MMA (mol)	X	Y	W	Z	F	G	η	ξ
0.0129	0.0056	2.30	24.75	0.32	13.88	0.128	1.710	10.41	0.78
0.0101	0.0085	1.19	12.50	0.32	14.81	0.057	0.777	8.37	0.61
0.0088	0.0099	0.89	9.33	0.29	14.89	0.042	0.559	7.18	0.54
0.0074	0.0128	0.58	6.15	0.27	16.30	0.023	0.316	5.37	0.39
0.0046	0.0141	0.33	3.85	0.21	18.76	0.011	0.152	3.25	0.23
0.0018	0.0169	0.11	1.21	0.16	35.40	0.001	0.006	0.22	0.05

$\alpha = 0.036$

Table 3 Data for group transfer copolymerization of MA with EMA including the extended Kelen-Tüdös parameters

MA (mol)	MMA (mol)	X	Y	W	Z	F	G	η	ξ
0.0155	0.0047	3.30	40.67	0.24	14.64	0.190	2.710	13.19	0.92
0.0121	0.0072	1.69	20.93	0.22	15.27	0.090	1.305	12.37	0.85
0.0088	0.0096	0.92	11.29	0.20	15.91	0.045	0.647	10.69	0.74
0.0055	0.0120	0.46	5.05	0.21	17.17	0.017	0.236	7.26	0.52
0.0041	0.0130	0.31	3.41	0.19	18.96	0.009	0.127	5.18	0.37
0.0022	0.0144	0.15	1.84	0.16	32.40	0.002	0.026	1.49	0.11

$\alpha = 0.0155$

Table 4 Data for group transfer copolymerization of MA with BMA including the extended Kelen-Tüdös parameters

MA (mol)	BMA (mol)	X	Y	W	Z	F	G	η	ξ
0.0155	0.0038	4.08	40.75	0.27	13.47	0.225	2.951	10.58	0.81
0.0121	0.0057	2.12	20.20	0.22	12.97	0.120	1.480	8.51	0.68
0.0088	0.0075	1.17	7.86	0.24	10.67	0.069	0.737	5.99	0.56
0.0055	0.0094	0.59	2.94	0.23	9.22	0.035	0.210	2.36	0.39
0.0022	0.0113	0.19	0.63	0.21	6.91	0.013	-0.054	-0.81	0.19

$\alpha = 0.054$

used as internal standard. The g.p.c. was performed on a Waters 208 spectrometer in THF, using polystyrene standards for calibration. The composition of the copolymer was determined using the resonances at $\delta = 3.6$ – 3.7 and 4.0 – 4.1 ppm to characterize the methyl and methylene protons adjacent to oxygen in the ester groups of the polymers, respectively. Determination of monomer reactivity ratios was carried out by using the extended Kelen-Tüdös method⁹.

RESULTS AND DISCUSSION

G.p.c. analysis

Because initiation incorporates a MMA unit in each

polymer chain, if the molecular weights of the products are sufficiently low, the compositions of copolymers determined by ¹H n.m.r. could be in error. The average molecular weight and molecular weight distribution of the products are shown in Table 1. It was found that the elution curves of the copolymers in g.p.c. were unimodal.

Monomer reactivity ratios

Most of the methods to determine the monomer reactivity ratio are appropriate at low conversions. Only the Mayo-Lewis¹⁰ and extended Kelen-Tüdös⁹ methods consider the drift in the comonomer and copolymer compositions with conversion. For the present group transfer and anionic copolymerization of acrylate with

Table 5 Data for group transfer copolymerization of MA with i-BMA including the extended Kelen–Tüdös parameters

MA (mol)	iBMA (mol)	X	Y	W	Z	F	G	η	ξ
0.0166	0.0031	5.36	39.58	0.22	8.47	0.552	4.555	6.96	0.84
0.0132	0.0049	2.69	20.24	0.24	9.09	0.245	2.117	6.10	0.71
0.0099	0.0068	1.46	9.72	0.27	8.86	0.124	0.984	4.35	0.55
0.0066	0.0087	0.76	4.76	0.25	9.03	0.058	0.416	2.60	0.36
0.0033	0.0105	0.31	1.95	0.21	10.18	0.019	0.093	0.77	0.16

$$\alpha = 0.102$$

Table 6 Data for anionic copolymerization of EA with MMA including the extended Kelen–Tüdös parameters

MA/B (mol)	BMA (mol)	X	Y	W	Z	F	G	η	ξ
0.0129	0.0056	2.29	17.99	0.26	9.49	0.199	1.790	7.58	0.84
0.0101	0.0085	1.20	9.738	0.21	10.0	0.097	0.874	6.52	0.72
0.0074	0.0113	0.65	4.406	0.24	8.93	0.055	0.381	4.14	0.60
0.0046	0.0141	0.33	2.047	0.25	9.93	0.021	0.105	1.81	0.36
0.0018	0.0169	0.11	0.571	0.21	9.31	0.007	-0.046	-1.05	0.16

$$\alpha = 0.037$$

Table 7 Data for anionic copolymerization of MA with EMA including the extended Kelen–Tüdös parameters

MA (mol)	iBMA (mol)	X	Y	W	Z	F	G	η	ξ
0.0166	0.0040	4.10	12.35	0.16	3.238	1.178	3.505	2.47	0.83
0.0133	0.0064	2.08	7.07	0.22	3.870	0.472	1.568	2.20	0.66
0.0099	0.0088	1.13	4.02	0.21	4.147	0.234	0.728	1.54	0.49
0.0066	0.0113	0.59	1.84	0.27	3.986	0.116	0.211	0.59	0.33
0.0033	0.0136	0.24	0.78	0.19	3.994	0.049	-0.054	-0.19	0.17

$$\alpha = 0.24$$

methacrylate, only data at relatively high conversion could be obtained due to the very high polymerization rate. It has been found that the most reliable method is the extended Kelen–Tüdös one¹¹, since one may simply use a linear graphic technique to calculate the reactivity ratio values with a very small error up to 60% conversion^{9,11,12}.

The extended Kelen–Tüdös method is expressed by the following equations:

$$\eta = (\gamma_1 + \gamma_2/\alpha)\xi - \gamma_2/\alpha$$

where

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F);$$

$$\alpha = (F_{\min} \cdot F_{\max})^{1/2}$$

$$F = Y/Z^2 \quad \text{and} \quad G = (Y - 1)/Z$$

$$Z = \log(1 - \zeta_1)/\log(1 - \zeta_2)$$

where

$$\zeta_2 = W(\mu + X)/(\mu + Y) \quad \text{and} \quad \zeta_1 = \zeta_2(Y/X);$$

where X and Y represent the molar ratios of monomer 1 to monomer 2 in the comonomer feed and the resulting copolymer, respectively. In addition, W equals the weight conversion of copolymerization, and μ is the ratio of molecular weight of monomer 2 to that of monomer 1.

Tables 2–5 contain the relevant data for monomer mixture composition, copolymer composition determined

Table 8 Reactivity ratios for the copolymerization of various acrylates with methacrylates by different synthetic techniques

M_1	M_2	Method	Temperature	γ_1	γ_2	Reference
MA	MMA	GTP	25	8.29	0.04	6
		Anionic	-30	4.5	0.1	13
		Radical	50	0.42	2.36	14
EA	MMA	GTP	25	14.15	0.01	This work
		Anionic	-40	9.67	0.11	This work
		Radical	60	0.47	1.83	15
MA	EMA	GTP	25	14.41	0.01	This work
		Anionic	-40	3.51	0.20	This work
MA	BMA	GTP	25	13.96	0.23	This work
MA	iBMA	GTP	25	8.66	0.08	This work
BA	MMA	GTP	25	6.74	0.14	6
		Radical	60	0.20	1.74	15

by ¹H n.m.r., and the associated parameters used in the extended Kelen–Tüdös procedure.

After finishing the extended Kelen–Tüdös plots, the intercepts at $\xi = 0$ and $\xi = 1$ of the ξ versus η plots give $\gamma_{EA} = 14.15$, $\gamma_{MMA} = 0.01$, $\gamma_{MA} = 14.41$, $\gamma_{EMA} = 0.01$, $\gamma_{MA} = 13.96$, $\gamma_{BMA} = 0.23$, $\gamma_{MA} = 8.66$ and $\gamma_{iBMA} = 0.08$, respectively. These data will confirm that acrylate is much more reactive than methacrylate in GTP, so much so that the relative reactivity ratio of methacrylate versus acrylate is scarcely distinguishable from zero. Such a large difference in the monomer reactivity ratio might indicate that the early polymer must be close to polyacrylate in character and the later be virtually polymethacrylate. So

the opportunity for mixed triads would occur only in the intermediate region and to a relatively small extent.

For the statistical anionic copolymerization of acrylate with methacrylate, some data are not available, so the monomer reactivity ratios of EA with MMA and of MA with EMA for anionic copolymerization were also determined. Tables 6 and 7 give the copolymerization data.

The monomer reactivity ratios are $\gamma_{MA} = 3.51$, $\gamma_{EMA} = 0.20$, $\gamma_{EA} = 9.67$ and $\gamma_{MMA} = 0.11$, respectively.

The results are summarized with those of previous work and other workers in Table 8, to compare the monomer reactivity ratios in different polymerization methods.

In radical copolymerization, methacrylate is more reactive than acrylate. In contrast, for anionic polymerization and GTP, acrylate is much more reactive than methacrylate; the ratios are quite different from unity and show a high similarity, so it is very possible that the GTP follows an anionic mechanism.

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