Statistical group transfer copolymerization. Monomer reactivity ratios for allyl methacrylate and n-butyl methacrylate

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Statistical copolymerizations have been performed for allyl methacrylate–butyl methacrylate systems using 1-methoxy-2-methyl-1-trimethylsilyloxypropene (initiator) and tris (dimethylamino) sulphonium bifluoride (catalyst) in tetrahydrofuran solution. Soluble allyl copolymers have been obtained by this method. The copolymer compositions were determined by ultraviolet spectroscopy and the results evaluated by the Kelen–Tüdos and Fineman–Ross methods. The reactivity ratios were found to be $r_{\mathrm{AMA}} = 2.35$, $r_{\mathrm{BMA}} = 0.08$ (Kelen–Tüdos) and $r_{\mathrm{AMA}} = 2.37$, $r_{\mathrm{BMA}} = 0.08$ (Fineman–Ross).

(Keywords: statistical copolymerization; group transfer polymerization; reactivity ratio; Kelen–Tüdos method; Fineman–Ross method)

Introduction

Group transfer polymerization (GTP)[1] bears a strong resemblance to anionic polymerization. A recent critical comparison by Müller[2] concluded that the mechanism of addition of the monomer to the active chain is very similar in both cases. Both techniques are useful for the same monomer, they have almost identical enthalpies and entropies of activation and produce polymers with similar tacticities.

Recently a great deal of work has been carried out comparing the reactivity ratios of both methods[2–4]. Here we report on our work on the allyl methacrylate–butyl methacrylate (AMA–BMA) system.

Another advantage of GTP is the production of soluble linear allyl copolymers. Radical polymerization of AMA results in either cyclic or crosslinked polymers[5]. Linear allyl polymers can be obtained by anionic polymerization but classical anionic polymerization of methacrylates using hindered alkyl lithium initiators requires low temperatures (−20 to −70°C)[6]. With GTP, soluble allyl copolymers are obtained at room temperature.

The allyl content of the copolymers was determined by ultraviolet (u.v.) spectroscopy at 242 nm. This method is based on the determination of the u.v. absorbances of homopolymers and copolymers at a previously determined wavelength[7].

Experimental

Polymerization procedure. The monomer mixture (20 ml), initiator, 1-methoxy-2-methyl-1-trimethylsilyloxypropene (MTS, 0.10 ml), and solvent, tetrahydrofuran (THF, 50 ml), were mixed together under an atmosphere of nitrogen. The catalyst, tris(dimethylamino) sulphonium bifluoride ($\mathrm{TASHF_2}$), was then added as a solution (0.10 M) in acetonitrile. The mixture immediately warmed slightly and after stirring for 1 min the polymer precipitated in a methanol–water mixture and then was dried *in vacuo* at room temperature overnight.

Copolymer analysis. The maximum absorbance values of poly (allyl methacrylate) and poly (butyl methacrylate) (5 mg $\mathrm{ml^{-1}}$ solution in chloroform) between 200 nm and 350 nm were determined. Both polymers gave maximum absorbance at 242 nm. A reference curve was obtained from the absorbances of known composition blends of the two homopolymers at 242 nm. Then the copolymer composition was found directly from this curve through its absorbance value at 242 nm (5 mg $\mathrm{l^{-1}}$ solution in chloroform).

Table 1 Data for copolymerization of AMA and BMA including Kelen–Tüdos parameters[8]

Copolymer	AMA mol. fraction (x) in monomer mixture	AMA mol. fraction (y) in copolymer	X	Y	G	F	η	ξ
1	0.05859	0.3309	0.0622	0.4945	−0.063	0.0078	−1.003	0.1245
2	0.1726	0.5298	0.2086	1.1267	0.0234	0.0386	0.2505	0.4123
3	0.2827	0.6088	0.3941	1.5560	0.1408	0.0998	0.9097	0.6447
4	0.5418	0.7811	1.1824	3.568	0.8510	0.3918	1.9046	0.8769

$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$ where $\eta = G/(\alpha + F)$, $\xi = F/(\alpha + F)$, $G = X(Y-1)/Y$, $F = X^2/Y$, $X = x/(1-x)$, $Y = y/(1-y)$ and α is the geometric mean of the lowest and the highest F values
$\alpha = 0.055$

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Results and discussion

Table 1 contains relevant data on the monomer mixture composition, copolymer composition and the associated parameters used in the Kelen–Tüdos procedure[8]. A least square plot of the data in the final two columns in the table gave $r_{\mathrm{AMA}} = 2.35$, $r_{\mathrm{BMA}} = 0.08$ (correlation coefficient $\gamma = 0.997$). Evaluation of the data according to Fineman–Ross[9] gave similar reactivity ratios: $r_{\mathrm{AMA}} = 2.37$, $r_{\mathrm{BMA}} = 0.08$ (correlation coefficient $\gamma = 0.999$).

The reactivity ratios determined up to 1990 were collected by Müller[2]. The recent work of Çatalgil and Jenkins agrees with the values reported for the methyl methacrylate–ethyl methacrylate (MMA–EMA) system. In that system the smaller monomer (MMA) was the more active one ($r_{\mathrm{MMA}} = 1.58 + 0.23$, $r_{\mathrm{EMA}} = 0.4 \pm 0.14$)[4]. In our case, the smaller monomer (AMA) was also the more active.

Another important aim is to obtain soluble allyl homo- and copolymers with GTP. Radical polymerization of AMA generally leads to gel formation or cyclic structures[5,6,10]. The anionic method would probably give linear allyl polymers, but requires very low temperatures. In addition to obtaining reactivity ratios for the group transfer copolymers another aim of this study was to contribute to the mechanistic studies on GTP. Currently GTP behaves very similarly to the anionic polymerization process. The reactivity ratios of similar anionic processes will probably give better insight into the cause of this similarity.

References

1 Webster, O. W., Hertler, W. R., Sogah, D. Y., Farnham, W. B. and Rajan Babu, T. V. *J. Am. Chem. Soc.* 1983, **105**, 5706
2 Müller, A. H. *Makromol. Chem. Symp.* 1990, **32**, 87
3 Jenkins, A. D., Tsartolia, E., Walton, D. R. M., Stejskal, J. and Kratochvil, P. *Polym. Bull.* 1988, **20**, 97
4 Çatalgil, H. and Jenkins, A. D. *Eur. Polym. J.* 1991, **27**, 651
5 Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G. and Kroschwitz, J. I. (Eds) 'Encyclopedia of Polymer Science and Engineering', Vol. 4, John Wiley and Sons, New York, 1986, p. 554
6 Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G. and Kroschwitz, J. I. (Eds) 'Encyclopedia of Polymer Science and Engineering', Vol. 2, John Wiley and Sons, New York, 1985, p. 1
7 Ramelov, U. and Baysal, B. M. *J. Appl. Sci.* 1986, **32**, 5865
8 Kelen, I. and Tüdos F. *J. Macromol. Sci. Chem.* 1975, **A9**, 1
9 Fineman, M. and Ross, S. *J. Polym. Sci.* 1950, **2**, 259
10 Sogah, D. Y., Hertler, W. R., Webster, O. W. and Cohen, G. *Macromolecules* 1987, **20**, 1473