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Statistical group-transfer copolymerisation
I. Monomer reactivity ratios for n-butyl methacrylate and methyl methacrylate

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Summary

Reactivity ratios have been determined for the statistical copolymerization of methyl methacrylate and n-butyl methacrylate by the group transfer techniques. The results are discussed in comparison with the corresponding radical and anionic processes.

Introduction

Simple binary copolymerisation is a fecund source of information on the reactivity of monomers and chain-carriers in chain-growth polymerisation. In particular, a great deal of effort has been devoted to the study of the reactivities of monomers and radicals by correlation of the monomer reactivity ratios with the structures of the reactants.[1] Moreover, given sufficient basic information about the reactivity ratios for different types of polymerisation mechanism, the reactivity ratios can be used diagnostically to determine which type of reactive intermediate is responsible for propagation in a particular case. In addition, a knowledge of reactivity ratios facilitates the calculation of the sequential arrangement of units in polymer chains, thus providing a picture of the overall architecture of the copolymer molecules.

Although the application of the Copolymer Composition Equation to radical and, to a much lesser extent, ionic systems is well-known, to date no examples of the analysis of Group Transfer Copolymerisation (GTC) have been reported, although such reactions have been performed[2-4] and applied to the synthesis of graft copolymers by copolymerisation of methyl methacrylate with a polystyrene macromonomer bearing a terminal methyl methacrylate unit.[5] The absence of reactivity ratio data is surprising because the mechanism of Group Transfer Polymerisation (GTP) proposed by the Du Pont group[2-4] is not universally accepted as an accurate representation of the process, which some chemists believe to be better regarded as an anionic polymerisation *déguisé*: a study of the reactivity ratios from GTC should provide useful evidence of the extent to which the process resembles simple anionic copolymerisation.

It will be necessary to carry out a careful study of the binary copolymerisation of a variety of acrylate, methacrylate, and related monomers in a number of different solvents in order fully to clarify the situation: as a first step, we have performed the GTC of methyl methacrylate (MM) and n-butyl methacrylate (BM), and we report here the determination of the monomer reactivity ratios for the reaction at 25°C in tetrahydrofuran solution.

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Experimental

(i) Materials

Tris(dimethylamino)sulfonium bifluoride was used as received (Aldrich). The monomers were each washed twice with 10% aqueous NaOH, dried over $MgSO_4$, distilled, dried over CaH_2, and distilled just before use. THF was stored over iron(II) sulfate, distilled, stored over sodium wire, refluxed over sodium and benzophenone, and distilled just before use. Acetonitrile was distilled over CaH_2. (1-methoxy-2-methyl-1-propenyloxy)-trimethylsilane (MTS) was prepared according to the literature.[6]

(ii) Copolymerisation procedure

To a solution of 0.1 ml of tris(dimethylamino)sulfonium bifluoride/acetonitrile (1 M) in 25 ml of anhydrous THF, was added (0.2 ml, 1 x 10^{-3} mmols) of MTS. Then, a mixture consisting of the required amounts of methyl methacrylate (MM) and n-butyl methacrylate (BM) was added slowly via a syringe. Upon addition of the monomers, the temperature rose ~ 20°C. After stirring for exactly 10 minutes, the solution was quenched, using a few drops of methanol. After removing the solvent by evaporation *in vacuo*, the residue was dissolved in CH_2Cl_2 and reprecipitated in petroleum ether, b.p. 30-40°C.

Results and Discussion

Direct application of the Kelen-Tüdős method[7] to our chemical composition data for GTC (Table 1) yields the monomer reactivity ratios r_{MM} = 0.47 ± 0.03 and r_{BM} = 0.30 ± 0.04 (Figure 1). If the drift of the monomer-mixture composition with the conversion of copolymerization is taken into account,[8] the corrected values r_{MM} = 0.44 ± 0.03 and r_{BM} = 0.26 ± 0.04 are obtained. Both monomer reactivity ratios differ from unity, showing that the formation of copolymer chains is not random, but is influenced by the structures of the reactants.

The relative reactivity of the end-unit of a growing chain towards the addition of monomers is likely to depend *inter alia* on the chemical nature of this terminal unit, which may include coordinated catalyst in some circumstances. In GTC one may therefore expect the values of the monomer reactivity ratios to be affected by the type of initiator or catalyst or both.

Table 1 Results of statistical group-transfer copolymerization of MM and BM (see Note A). Runs taken to 20% conversion.

Sample	y	x
1	0.20	0.34
2	0.30	0.37
3	0.40	0.48
4	0.50	0.55
5	0.60	0.57
6	0.70	0.68
7	0.80	0.74

Note A. y and x are the mole fractions of MM in the initial mixture of monomers and in the copolymer, respectively.

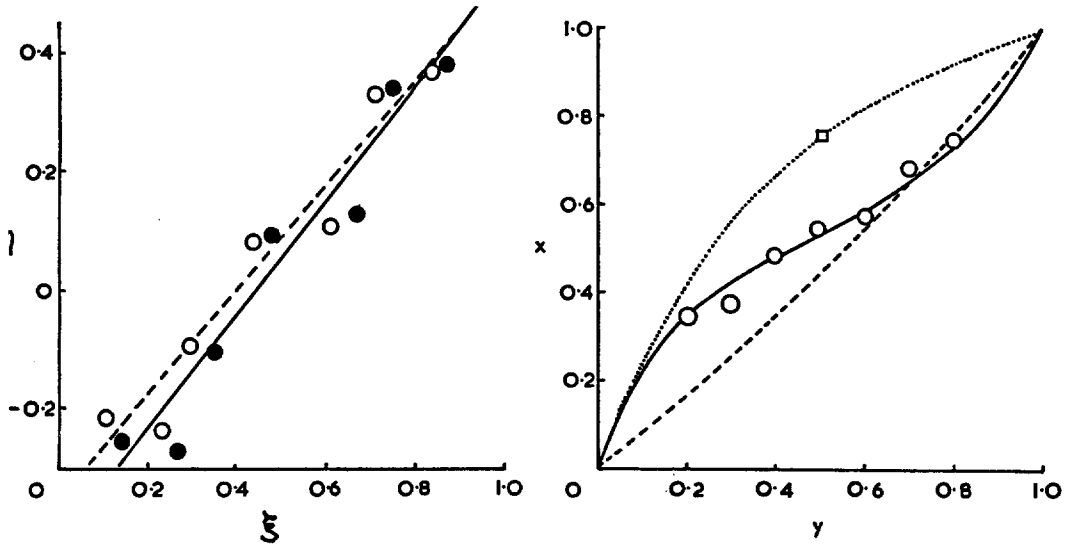

Figure 1. Determination of the monomer reactivity ratios r_{MM} and r_{BM} by the method of Kelen and Tüdős[7]: $\eta = (r_{MM}+r_{BM}/\alpha)\xi - r_{BM}/\alpha$, where $\eta = G/(\alpha+F)$, $\xi = F/(\alpha+F)$; $F = Y^2X$, $G = Y(X-1)/X$, and $X = x(1-x)$, $Y = y/(1-y)$. x and y are the mole fractions of MM in the copolymer and in the initial mixture of monomers, respectively. α is the geometric mean of the lowest and the highest F-values.
(○), points for $\alpha = 1$; (●), points for $\alpha = 0.84$, the optimum value, according to Kelen and Tüdős[7].

Figure 2. Comparison of statistical copolymerization diagrams for the binary monomer system MM and BM by GTC (full line), radical copolymerization (broken line) and anionic copolymerization (dotted line). x and y are, respectively, the compositions of the copolymer and of the monomer mixture (mole fraction MM in both cases).

For the radical copolymerization of MM and BM, the monomer reactivity ratios were reported by Bevington and Harris[9] to be $r_{MM} = 0.79$ and $r_{BM} = 1.27$ (60 °C, azobisisobutyronitrile, 5% conversion) and by Musha et al.[10] to be $r_{MM} = 1.20$ and $r_{BM} = 1.27$ (60°C, dibenzoylperoxide). The only quantitative information about the statistical anionic copolymerization of the two monomers is a report[11] that, in toluene, an equimolar feed composition produces a copolymer containing 75 mole % MM. It can be shown that this result can not arise if both reactivity ratios are less than unity. If one of them is greater, and one less than, unity, calculation shows that r_{MM} must have a minimum value of 2.0; if it is assumed that the system corresponds to "ideal" copolymerization, it follows that $r_{MM} = 3$ and $r_{BM} = 1/3$. Although necessarily tentative, these values have been used to gain an indication of the cause of the anionic reaction. Comparison of the copolymerization diagrams (Figure 2) shows substantial differences in the compositions of copolymers formed at low MM contents in the group transfer, anionic, and classical radical copolymerization processes.

As GTC proceeds, the composition of the monomer mixture changes (except, of course, for the azeotropic composition). One of the monomers is gradually depleted from the monomer mixture because of its preferential incorporation into the copolymer (Figure 2). Consequently, the copolymer composition changes as the (living) chain grows, and a tapering effect must be operative. This is a basic difference compared to classical statistical copolymerization where macromolecules with different copolymerizations are formed at different conversions, giving rise to conversion chemical heterogeneity; this is unlikely to occur with GTC.

It is clearly desirable to carry out more studies of this kind, especially on systems for which more extensive data relating to conventional anionic polymerization are available; we expect to submit further reports in the near future.

References

1. A.D. Jenkins, Advances in Free Radical Chemistry, 2, 117 (1967).
2. O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham, T.V. Rajan Babu, J. Amer. Chem. Soc., 105, 5706 (1983).
3. W.R. Hertler, A.C.S. Polym. Preprints, 27(1), 165 (1986).
4. D.Y.Sogah, W.R.Hertler, O.W.Webster, G.M.Cohen, Macromolecules, 20,1473 (1987).
5. R. Asami, M. Takaki, Y. Moriyama, Polym. Bull., 16, 125 (1986).
6. C. Ainsworth, F. Chen, Kuo Yu-Weng, J. Organomet. Chem., 46, 59 (1972).
7. T. Kelen and F. Tüdős, J. Macromol. Sci. (Chem.), A9, 1 (1975).
8. T. Kelen, F. Tüdős, B. Turcsányi and J.P. Kennedy, J. Polym. Sci., Polym. Chem. Ed., 15, 3047 (1977).
9. J.C. Bevington and D.O. Harris, J. Polym. Sci., B5, 799 (1967).
10. Y. Musha, Y. Hori, Y. Sato, M. Katayama, Nihon Daigaku Kogakubu Kiyo, Bunrui A, 26, 175 (1985); C.A., 103, 178669h (1985)
11. Z.A. Azimov, A.A. Korotkov, S.P. Mitsengendler, Vysokol. Soed., A10, 2145 (1968).

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