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# Group-transfer copolymerization

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Statistical copolymerization has been performed for five binary systems using 1-methoxy-2-methyl-1-trimethylsilyloxy propene (initiator) and tetrabutylammonium bibenzoate (catalyst) in tetrahydrofuran solution. The copolymer compositions were determined by elemental analysis for nitrogen and the results evaluated by the Kelen–Tudos method. The monomer pairs concerned are (1) acrylonitrile (AN) and methyl methacrylate (MMA), (2) AN and ethyl methacrylate (EMA), (3) AN and butyl methacrylate (BMA), (4) AN and butyl acrylate (BA), (5) AN and dibutyl maleate (DBM). The reactivity ratios determined in this study are: (1) $\gamma_{AN} = 10.22$, $\gamma_{MMA} = 0.07$; (2) $\gamma_{AN} = 5.68$, $\gamma_{EMA} = 0.16$; (3) $\gamma_{AN} = 8.59$, $\gamma_{BMA} = 0.09$; (4) $\gamma_{AN} = 4.08$, $\gamma_{BA} = 0.06$; (5) $\gamma_{AN} = 1.38$, $\gamma_{DBM} = 0.06$. The copolymers were characterized by g.p.c., i.r. and $^1$H n.m.r.

**(Keywords: group transfer polymerization; statistical copolymerization; reactivity ratio; Kelen–Tudos method)**

## *Introduction*

Simple binary copolymerization can give sufficient basic information about the reactivity ratios for different types of polymerization mechanism. Recently, some work has been carried out comparing the reactivity ratios for group-transfer polymerization and anionic polymerization[1–3].

Acrylonitrile and (meth)acrylate copolymers are industrially important copolymers. Copolymerization of acrylates with methacrylates by GTP presents special problems due to the disparate reactivities of the two types of monomer[7]; to date no examples of statistical group-transfer copolymerization of acrylonitrile with methacrylate have been reported. We report here determination of the monomer reactivity ratios of AN and methacrylate for group-transfer copolymerization at 25°C in tetrahydrofuran solution. The results are discussed in comparison with the corresponding radical and anionic processes.

## *Experimental*

*Materials.* 1-Methoxy-2-methyl-1-trimethylsilyloxy-propene (MTS) was prepared according to the literature[4], and tetrabutylammonium bibenzoate (TBABB) was prepared according to the literature[5].

*Copolymerization procedure.* The monomer mixture (2.0 ml), the initiator 1-methoxy-2-methyl-1-trimethyl-silyloxypropene (MTS) (0.010 ml), and tetrahydrofuran (THF) as solvent (10 ml) were mixed under an atmosphere of $N_2$. The catalyst, tetrabutylammonium bibenzoate (TBABB), was then added as a solution (0.2 M) in acetonitrile. The mixture immediately warmed, the temperature rose ~ 20°C. 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 DMF solution into petroleum ether, and then dried *in vacuo* at 40°C overnight. Pure copolymers were confirmed by *FT*i.r., $^1$H n.m.r and g.p.c (*Tables 1* and *2*).

*Polymer analysis.* Elemental analysis for nitrogen provided the necessary compositional information.

*Measurements.* $^1$H n.m.r. spectra were recorded on a Varian Unity plus-500 spectrometer for 5 w/v % polymer solutions in $CDCl_3$ at 298 K, with TMS as internal standard. I.r. measurements were performed using polymer films on NaCl plates (5DXFT-IR spectrophotometer). G.p.c. was determined on a Waters 208 spectrometer in THF, using polystyrene standards for calibration. Elemental analysis was performed on a Perkin–Elmer 240 B analyzer.

## *Results and discussion*

*Tables 3–7* contain the relevant data for monomer mixture composition, copolymer composition, and the associated parameters used in the Kelen–Tudos procedure[6]. Direct application of the Kelen–Tudos method to our chemical composition data for group-transfer copolymerization of AN and (meth)acrylates yields the monomer reactivity ratios: $\gamma_{AN} = 10.22$ and $\gamma_{MMA} = 0.07$; $\gamma_{AN} = 5.68$ and $\gamma_{EMA} = 0.16$; $\gamma_{AN} = 8.59$ and $\gamma_{BMA} = 0.09$; $\gamma_{AN} = 4.08$ and $\gamma_{BA} = 0.06$; $\gamma_{AN} = 1.38$ and $\gamma_{DBM} = 0.06$, respectively. The results presented here show that AN is much more active in group-transfer copolymerization than the ester monomers.

For the radical copolymerization of AN and MMA, the monomer reactivity ratios were reported by Gerken *et al.*[8] to be $\gamma_{AN} = 0.29$ and $\gamma_{MMA} = 1.53$. For statistical anionic copolymerization of the two monomers, the monomer reactivity ratios[9] are $\gamma_{AN} = 7$, $\gamma_{MMA} = 0.39$ (−8°C, n-BuLi) and $\gamma_{AN} = 7.9$, $\gamma_{MMA} = 0.25$ (−30°C, Na–$NH_3$). For the radical copolymerization of AN and EMA, the monomer reactivity ratios were reported by Kapur *et al.*[10] to be $\gamma_{AN} = 0.18$ and $\gamma_{EMA} = 1.41$; for AN and BMA[11] $\gamma = 0.29$, $\gamma_{BMA} = 0.98$; and for AN and

**Table 1** I.r. and $^1$H n.m.r. data for copolymers

| Copolymer | I.r. ($\nu$, cm$^{-1}$) |  | $^1$H n.m.r. ($\delta$, ppm) |  |  |
|---|---|---|---|---|---|
|  | C ≡ N | C = O | $\overset{\mathrm{CN}}{\underset{\mathrm{H}}{-\mathrm{C}-}}$ | $\overset{\mathrm{CO_2R}}{\underset{\mathrm{H(CH_3)}}{-\mathrm{C}-}}$ | $\overset{\mathrm{CO_2CH}}{\underset{\mid}{-\mathrm{C}-}}$ |
| P(AN-*co*-MMA) | 2244.2 | 1724.4 | 3.41 | 1.01 | 3.63 |
| P(AN-*co*-EMA) | 2244.4 | 1724.2 | 3.40 | 0.98 | 3.50 |
| P(AN-*co*-BMA) | 2245.2 | 1724.2 | 3.40 | 0.96 | 3.45 |
| P(AN-*co*-BA) | 2244.1 | 1727.6 | 3.45 | 2.42 | 4.10 |
| P(AN-*co*-DBM) | 2244.6 | 1729.3 | 3.85 | 2.78 | 4.32 |

**Table 2** Group-transfer copolymerization of AN ($M_1$) with ester monomer ($M_2$)

| Entry | $M_2$ | $M_1/M_2$ | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_W \times 10^{-3}$ | *D* | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | MMA | 1.96 | 7.21 | 8.36 | 1.16 | 32 |
| 2 | MMA | 0.54 | 6.78 | 7.73 | 1.14 | 21 |
| 3 | EMA | 2.32 | 4.90 | 6.71 | 1.37 | 35 |
| 4 | EMA | 0.63 | 4.17 | 5.46 | 1.31 | 27 |
| 5 | BMA | 2.93 | 6.73 | 8.41 | 1.25 | 38 |
| 6 | BMA | 0.43 | 5.67 | 6.80 | 1.20 | 23 |
| 7 | BA | 2.65 | 8.19 | 12.0 | 1.47 | 29 |
| 8 | BA | 0.72 | 7.36 | 8.90 | 1.28 | 20 |
| 9 | DBM | 6.16 | 6.95 | 12.58 | 1.81 | 42 |
| 10 | DBM | 3.45 | 3.16 | 7.55 | 2.39 | 28 |

**Table 3** Data for copolymerization of AN and MMA, including Kelen–Tudos parameters

| Entry | AN (mol) | MMA (mol) | *N* (%) | *X* | *Y* | *G* | *F* | $\eta$ | $\zeta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0213 | 0.0056 | 25.14 | 3.78 | 38.30 | 3.68 | 0.370 | 7.80 | 0.78 |
| 2 | 0.0167 | 0.0085 | 24.14 | 1.97 | 20.24 | 1.87 | 0.190 | 6.40 | 0.65 |
| 3 | 0.0122 | 0.0113 | 22.78 | 1.08 | 11.90 | 0.99 | 0.098 | 4.95 | 0.49 |
| 4 | 0.0076 | 0.0141 | 20.23 | 0.54 | 6.22 | 0.45 | 0.047 | 3.02 | 0.32 |
| 5 | 0.0046 | 0.0160 | 15.57 | 0.29 | 3.00 | 0.19 | 0.028 | 1.48 | 0.22 |
|  | $\alpha = 0.102$ |  |  |  |  |  |  |  |  |

**Table 4** Data for copolymerization of AN and EMA, including Kelen–Tudos parameters

| Entry | AN (mol) | BMA (mol) | *N* (%) | *X* | *Y* | *G* | *F* | $\eta$ | $\zeta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0213 | 0.0048 | 24.39 | 4.44 | 26.36 | 4.27 | 0.75 | 4.44 | 0.78 |
| 2 | 0.0167 | 0.0072 | 22.90 | 2.32 | 14.14 | 2.16 | 0.38 | 3.65 | 0.64 |
| 3 | 0.0152 | 0.0080 | 22.04 | 1.90 | 10.90 | 1.73 | 0.33 | 3.19 | 0.61 |
| 4 | 0.0122 | 0.0096 | 20.12 | 1.27 | 6.92 | 1.09 | 0.23 | 2.46 | 0.52 |
| 5 | 0.0076 | 0.0120 | 18.01 | 0.63 | 4.64 | 0.49 | 0.09 | 1.62 | 0.30 |
| 6 | 0.0046 | 0.0136 | 12.58 | 0.34 | 1.96 | 0.17 | 0.06 | 0.63 | 0.22 |
|  | $\alpha = 0.212$ |  |  |  |  |  |  |  |  |

BA[12] to be $\gamma_{AN} = 0.71$, $\gamma_{BA} = 1.17$. This means that the ester monomers are more active in radical copolymerization and AN is much more active in anionic copolymerization and group-transfer copolymerization.

Like that of aninoic copolymerization[9], the rates of group-transfer copolymerization depend strongly upon comonomer composition; the comonomer mixture highest in acrylonitrile gives the most rapid polymerization.

**Table 5** Data for copolymerization of AN and BMA, including Kelen–Tudos parameters

| Entry | AN (mol) | BMA (mol) | $N$ (%) | $X$ | $Y$ | $G$ | $F$ | $\eta$ | $\zeta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0213 | 0.00378 | 24.97 | 5.63 | 46.94 | 5.51 | 0.68 | 6.37 | 0.79 |
| 2 | 0.0167 | 0.00567 | 23.94 | 2.95 | 26.31 | 2.84 | 0.33 | 5.51 | 0.64 |
| 3 | 0.0091 | 0.00881 | 20.41 | 1.03 | 9.18 | 0.92 | 0.12 | 3.03 | 0.39 |
| 4 | 0.0061 | 0.01007 | 17.78 | 0.60 | 5.52 | 0.49 | 0.07 | 1.97 | 0.26 |
| 5 | 0.0046 | 0.01070 | 15.15 | 0.43 | 3.60 | 0.31 | 0.05 | 1.32 | 0.21 |
| | $\alpha = 0.184$ | | | | | | | | |

**Table 6** Data for copolymerization of AN and BA, including Kelen–Tudos parameters

| Entry | AN (mol) | BMA (mol) | $N$ (%) | $X$ | $Y$ | $G$ | $F$ | $\eta$ | $\zeta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0213 | 0.0042 | 23.68 | 5.07 | 21.13 | 4.83 | 1.22 | 2.96 | 0.75 |
| 2 | 0.0167 | 0.0063 | 21.75 | 2.65 | 11.31 | 2.42 | 0.62 | 2.35 | 0.60 |
| 3 | 0.0152 | 0.0070 | 21.26 | 2.17 | 10.00 | 1.95 | 0.47 | 2.22 | 0.53 |
| 4 | 0.0122 | 0.0084 | 19.31 | 1.45 | 6.60 | 1.23 | 0.32 | 1.68 | 0.44 |
| 5 | 0.0076 | 0.0105 | 15.84 | 0.72 | 3.65 | 0.52 | 0.14 | 0.95 | 0.25 |
| | $\alpha = 0.41$ | | | | | | | | |

**Table 7** Data for copolymerization of AN and DBM, including Kelen–Tudos parameters

| Entry | AN (mol) | DMA (mol) | $N$ (%) | $X$ | $Y$ | $G$ | $F$ | $\eta$ | $\zeta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0259 | 0.0013 | 22.77 | 19.58 | 27.17 | 18.86 | 13.84 | 0.93 | 0.69 |
| 2 | 0.0213 | 0.0026 | 19.72 | 8.10 | 12.70 | 7.46 | 5.17 | 0.65 | 0.45 |
| 3 | 0.0191 | 0.0031 | 17.96 | 6.22 | 9.14 | 5.54 | 4.23 | 0.52 | 0.40 |
| 4 | 0.0152 | 0.0044 | 14.91 | 3.46 | 5.63 | 2.85 | 2.13 | 0.34 | 0.25 |
| | $\alpha = 6.33$ | | | | | | | | |

It is clear that group-transfer polymierization and anionic polymerization are very similar with respect to the identity of the active monomers. It is hoped that further studies of statistical copolymerization initiated by both GTP and anion will be reported in order to clarify the mechanism of GTP.

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