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.\textsuperscript{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\textsuperscript{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.\textsuperscript{5} The absence of reactivity ratio data is surprising because the mechanism of Group Transfer Polymerisation (GTP) proposed by the Du Pont group\textsuperscript{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 \textit{d{\`e}guis{\`e}}: 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 MgSO₄, distilled, dried over CaH₂, 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 CaH₂. (1-methoxy-2-methyl-1-propenyl)trimethylsilane (MTS) was prepared according to the literature.

(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 CH₂Cl₂ and reprecipitated in petroleum ether, b.p. 30-40°C.

Results and Discussion

Direct application of the Kelen-Tüdős method to our chemical composition data for GTC (Table 1) yields the monomer reactivity ratios \( r_{MM} = 0.47\pm0.03 \) and \( r_{BM} = 0.30\pm0.04 \) (Figure 1). If the drift of the monomer-mixture composition with the conversion of copolymerization is taken into account, the corrected values \( r_{MM} = 0.44\pm0.03 \) and \( r_{BM} = 0.26\pm0.04 \) 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>y</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.34</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
<td>0.37</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>0.48</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>0.55</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>0.70</td>
<td>0.68</td>
</tr>
<tr>
<td>7</td>
<td>0.80</td>
<td>0.74</td>
</tr>
</tbody>
</table>

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