The free radical copolymerization characteristics of α-methylene γ-butyrolactone

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The free radical copolymerization of α-methylene γ-butyrolactone (α-MBL, I) has been studied at 60°C, with methyl methacrylate, styrene, acrylamide, acrylonitrile and vinylene carbonate, respectively. The reactivity ratios thus determined generally establish the high reactivity of α-MBL as a comonomer.

INTRODUCTION

α-methylene γ-butyrolactone[1-3] (α-MBL, I) has been known in recent years as the parent member of a group of biologically active, naturally occurring sesquiterpene lactones. From a polymer chemist's point of view, α-MBL may be visualized as a cyclic analogue of methyl methacrylate (2) and hence is expected to be a reactive vinyl monomer.
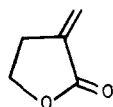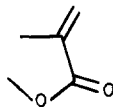
I   2

Very little information exists on the polymerization characteristics of this monomer except for a brief description of its free radical polymerization in a patent by McGraw.[4] Some aspects of free radical and anionic polymerization of α-MBL and a study of the configurational microstructure of the resulting polymers by high resolution ^{13}C n.m.r. have been investigated recently by the present author.[5] In general, copolymerization reactivity ratios offer an insight into the steric, polar and resonance factors characterizing the reactivity of a monomer and its radical. Towards this objective, the copolymerization behaviour of α-MBL with some common vinyl monomers has been studied.

EXPERIMENTAL

α-methylene γ-butyrolactone was synthesized from γ-butyrolactone using Ksander's[1] method *et al.*[6] Methyl methacrylate, styrene, acrylonitrile, and vinyl acetate (all from Aldrich) were distilled free from inhibitor just prior to use. Acrylamide (Electrophoresis grade, Polysciences Inc) was used without further purification. Vinylene carbon carbonate was prepared according to the literature procedure. Copolymerization of α-MBL with various comonomer was carried out in bulk, with 0.5% (W/W) AIBN as initiator at 60°C in polymerization tubes, degassed and sealed under vacuum. The conversions were always kept low (<5%) and the copolymers were precipitated in non-solvents such as

methanol or ether, washed free of monomers and dried under vacuum. In the case of acrylamide, copolymerizations were carried out in DMF as solvent. Compositions of the copolymers were determined by ^{1}H n.m.r. analysis on a varian HA-100 instrument or by elemental analysis. The n.m.r. spectra were normally recorded on 15-20% (W/W) copolymer solutions in DMSO-d_6 at 150°C. For α-MBL-MMA copolymers, integrations of the peaks at δ4.3ppm (-OCH$_2$-) and δ3.6ppm (-OCH$_3$) were used to estimate the contents of α-MBL and MMA comonomer units, respectively. For α-MBL-styrene copolymers integration of peaks at δ4ppm (-OCH$_2$-) and δ7.2ppm (aromatic) were used to measure α-MBL and styrene monomer units, respectively.

α-MBL acrylamide copolymers were analysed for nitrogen (x%) and the mole fraction of α-MBL in the copolymer (P_1) was calculated from the relationship:

$$P_1 = \frac{14 - 0.71x}{14 + 0.27x}$$

α-MBL acrylonitrile copolymers were also analysed for nitrogen (x%) and P_1 was calculated from the relationship:

$$P_1 = \frac{14 - 0.53x}{14 + 0.45x}$$

RESULTS AND DISCUSSION

The free radical copolymerization of α-methylene γ-butyrolactone (α-MBL) with methyl methacrylate, styrene, acrylamide, acrylonitrile and vinylene carbonate, respectively, was studied with AIBN as initiator at 60°C (*Table 4*). The copolymers isolated at low conversions (<5%) were analyzed either by ^{1}H n.m.r. or by elemental analysis. The copolymerization diagrams indicating the instantaneous copolymer composition against feed composition for each comonomer system are shown in *Figure 1*.

The copolymerization reactivity ratios were determined by the Fineman–Ross method[7] (*Table 1*). With methyl methacrylate, a monomer structurally close to α-MBL, the reactivity ratios of $r_1 = 1.67$ and $r_2 = 0.6$ were found, indicating that the two monomers form an ideal, random
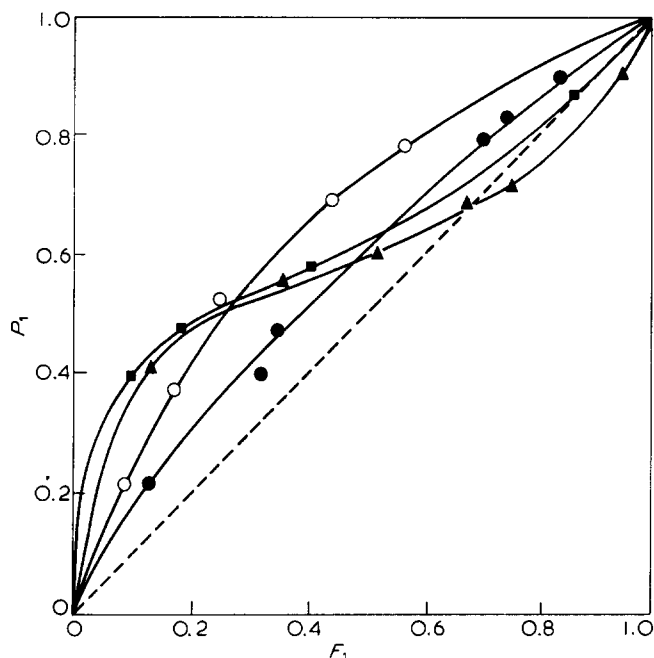
Figure 1 Copolymerization of α-Methylene γ-butyrolactone (M_1) with ▲—Styrene; ○—Acrylamide; ●—Methyl methacrylate; ■—Acrylonitrile. F_1 and P_1 are mole fractions of M_1 in the feed and the copolymer; the points respresent experimental data and the lines represent the theoretical composition curves calculated from the reactivity ratios of *Table 1*

Table 1 Reactivity ratios[a] for the free radical copolymerization of α-methylene γ-butyrolactone (M_1) with various comonomers (M_2) (AIBN, 60°C)

Comonomer (M_2)	r_1	r_2
Methyl methacrylate[b]	1.67	0.6
Styrene[b]	0.7	0.09
Acrylamide[c]	2.85	0.3
Acrylonitrile[c]	1.1	0.09
Vinylene carbonate[b]	Very large[d]	0

[a] determined by the Fineman–Ross method; ie from the linear plots of $F_1(P_2-P_1)/F_2P_1$ vs $F_1{}^2P_2/F_2{}^2P_1$ where F_1 and P_1 are the mole fractions of monomer 1 in the feed ad the copolymer, respectively

[b] copolymer composition determined by ^{1}H n.m.r. analysis

[c] copolymer composition determined by elemental analysis

[d] essentially homopolymer of α-MBL with no detectable incorporation of vinylene carbonate

copolymer, since $r_1r_2 = 1.02$. Assuming the resonance stabilization of the radicals in both cases is similar, the slightly higher reactivity of α-MBL to both its own radical $(r_1 = 1.67)$ and to the poly (MMA) radical $(1/r_2 = 1.67)$ may be attributed to the steric factors. The methylene groups of α-MBL offer less steric interaction in the transition state than the methyl groups of MMA. The reactivity ratios for α-MBL styrene system were found to be $r_1 = 0.7$ and $r_2 = 0.9$, indicating some alternating tendency. Azeotropic copolymerization occurs in the system at a feed composition of 70 mol% α-MBL (*Figure 1*). α-MBL forms nearly ideal random copolymers with acrylamide as indicated by the values of $r_1 = 2.85$ and $r_2 = 0.3$. The instantaneous copolymer compositions are rich in α-MBL at all feed compositions indicating the higher reactivity of the monomer to both its own polymer radical as well as to the polyacrylamide radical. The copolymerization with acrylonitrile suggests some alternating tendency which cannot be rationalized at

this moment. Due to the low reactivity of vinylene carbonate, a characteristic of 1, 2 disubstituted olefins, copolymerization of α-MBL resulted in nearly homopolymers with no detectable vinylene carbonate incorporation in the range of the feed compositions studied ($F_1 = 0.1$ to 0.9). Estimation of $Q-e$ parameters using the literature values[8] of MMA ($A = 0.74$, $e = 0.4$), Styrene ($Q = 1$, $e = 0.8$) and Acrylamide ($Q = 1.12$ and $e = 1.19$) gave for α-MBL values of $Q = 1.23$, $e = 0.4$, $Q = 2.9$, $e = 0.86$ and $Q = 2.32$, $e = 0.79$, respectively. To summarize the results of copolymerization experiments establish the high reactivity of α-MBL as a comonomer which is comparable to and, in fact, somewhat higher than that of MMA.

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