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Copolymerization of 2-methacryloxytropone with methyl methacrylate and ethyl acrylate

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Summary

2-Methacryloxytropone was synthesized via reported methods and it's free radical initiated copolymerization with methyl methacrylate or ethyl acrylate was investigated. The 2-methacryloxytropone was found to be the more reactive monomer in both cases, however the difference in reactivity was more pronounced in the ethyl acrylate case.

Introduction

The synthesis and polymerization of 2-methacryloxytropone was first reported by Cornell and Donaruma in 1965 (1). These authors investigated the homopolymerization behavior of the monomer and the biological activity of the monomer and the homopolymer. No investigation of the copolymerization behavior of this monomer has, to our knowledge, been conducted. In addition, we have an interest in the synthesis of polymers and copolymers that have functionalities capable of participating in post polymerization reactions (2,3). We thought therefore, that it would be of interest to investigate the synthesis and properties of copolymers of 2-methacryloxytropone (MOT). This paper presents our initial results concerning copolymerization with two commonly used monomers, methyl methacrylate and ethyl acrylate.

Experimental

General

All solvents and other chemicals used in this study were reagent grade (Aldrich) and were used as received. ^{1}H-NMR spectra were recorded with a Varian Gemini 300 FT NMR. The spectra were obtained from 8-10% w/v solutions of polymer in $CDCl_3$. Tetramethylsilane was used as an internal standard. Molecular weights were measured with a GPC equipped with a Waters 510 Pump, a refractive index detector and two Polymer Labs linear columns (total length = 180 cm). Tetrahydrofuran was used as the eluent and numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Monomer Synthesis

The monomer was synthesized as previously reported (1) and was purified by recrystallization from hexane. Yield = 58%, m.p. = 75-76°, lit. m.p. = 78-79°.

Polymerizations

Because MOT was not soluble in all proportions in MMA or EA, the copolymerizations were performed using dry N,N-dimethylformamide as a solvent. A typical polymerization was performed as follows: the desired amounts of the comonomers were weighed into a clean, dry screw cap vial. The solvent, 1.0 ml, was then added followed by 0.5 wt % initiator (70% benzoyl peroxide). The solution was sparged with dry N_2 while cold (evaporation loss $<$ 1 wt %) and the vial was tightly sealed with a teflon lined screw cap. The vial was then placed in a thermostated waterbath at 75°C for the desired length of time. Polymerizations were terminated by removing the vials from the bath, cooling to ambient temperature with cold water and adding cold CH_3OH to the contents of the vial. The copolymers were purified by reprecipitating them twice from $CHCl_3$ solution into CH_3OH. The copolymers were dried in vacuo at 30°C for 72h and then weighed to determine conversion.

Results and Discussion

The feed charges, polymerization times and polymer compositions are summarized in Table 1.

Because of the relatively high conversions obtained for the MOTM series of copolymers, the reactivity ratios were calculated using an integral form of the Mayo-Lewis equation (4,5). This form of the equation allows consideration of conversion in the calculation of reactivity ratios. The values obtained for the MOT/MMA monomer pair (MOT = M_1) were; $r_1 = 1.17 \pm .35$ and $r_2 = 0.68 \pm .20$. The values obtained for the MOT/EA monomer pair (MOT = M_1) were; $r_1 = 3.1 \pm .7$ and $r_2 = 0.37 \pm .10$. The values obtained show that MOT is the more reactive monomer in each of these copolymerizations i.e. no matter what the growing chain end it prefers to add MOT. Some monomer mean sequence lengths, μ_1 and μ_2 were calculated using Pyun's equations (6), the results are presented in Table 2.

TABLE 1

Summary of Polymerization Results

Co-polymer	Co-monomer	M_f of MOT in feed	Pzn Time (hr)	% Conv.	M_f of MOT in Copolymer	M_n	M_w/M_n
MOTM1	MMA	0.041	4.5	23.3	0.047	35000	1.85
MOTM2	MMA	0.011	4.5	29.5	0.12	23000	1.70
MOTM3	MMA	0.021	4.5	9.4	0.27	18300	1.48
MOTM4	MMA	0.024	4.5	13.9	0.30	15800	1.33
MOTM5	MMA	0.038	4.5	13.9	0.45	-	-
MOTM6	MMA	0.060	4.5	25.6	0.63	2700	1.78
MOTE1	EA	0.037	3.5	10.2	0.082	7000	1.79
MOTE2	EA	0.17	3.5	9.8	0.34	3000	1.63
MOTE3	EA	0.21	3.5	10.8	0.43	2800	1.57
MOTE4	EA	0.36	3.5	8.4	0.62	2700	1.52
MOTE5	EA	0.49	3.5	6.4	0.74	2600	1.46
MOTE6	EA	0.65	3.5	10.5	0.83	2300	1.39

TABLE 2

Monomer Mean Sequence Lengths

Polymer	M_f of MOT in Copolymer	μ_1	μ_2
MOTM1	0.047	1.06	14.79
MOTM3	0.27	1.43	2.84
MOTM5	0.45	1.96	1.83
MOTE1	0.082	1.28	5.14
MOTE3	0.43	3.34	1.49
MOTE5	0.74	9.82	1.13

Conclusions

The copolymerization of methacryloxytropone with methyl methacrylate and ethyl acrylate was investigated. The methacryloxytropone monomer was found to be the most reactive monomer in both cases, although the difference in reactivity is less pronounced in the MMA case than for the EA comonomer. This is not unexpected given that MMA and methacryloxytropone are both methacrylates. Further evidence of the similarity in reactivity of MMA and methacryloxytropone is shown in the relatively long sequence lengths of MMA possible in copolymerizations with low to moderate feed concentrations of the tropone monomer.

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