Organotin Polymers.I. Copolymerization on Tributyltin Methacrylate with (Hydroxy)alkyl Methacrylates

J. R. DHARIA, C. P. PATHAK, G. N. BABU,* and S. K. GUPTA,
Center for Environmental Science and Engineering, Indian Institute of Technology, Powai, Bombay 400 076, India

Synopsis

Copolymers of tributyltin methacrylate (M_1) with cyclohexyl methacrylate, ethoxyethyl methacrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate were synthesized in solution at 55°C utilizing azobisisobutyronitrile initiator. Copolymer compositions were determined by tin analysis; monomer reactivity ratios were calculated by Kelen-Tüdös method. Since the reactivity ratios indicate the distribution of different monomer units in the polymer chain, the measured values are compared and discussed. Preliminary results of the biotoxicity studies on some of the copolymers are also reported.

INTRODUCTION

The copolymerization of methacrylic or acrylic esters with tributyltin (meth)acrylates has been the subject of much interest because of the applications of these polymers as antifouling coatings and fungicides.[1-4] Although there have been several copolymer systems reported in the literature, little is known about the role played by the comonomer on the rate of the release of tin moiety and the biocidic properties. Recently Zeldin and Lin reported that stereochemistry of polymers plays an important role on the rate of release of organotin units.[5] In the present investigation we report the copolymerization of functional and alkyl methacrylates with tributyltin methacrylate. The presence of functional units in the copolymer can be utilized to selectively cross-link the polymers so that the rate of release of tin moiety can be controlled.

EXPERIMENTAL

Tributyltin methacrylate (TBTM) was prepared according to a previously reported procedure.[2] Cyclohexyl methacrylate (CMA), ethyl methacrylate (EMA), 2-ethoxyethyl methacrylate (EEMA), 2-hydroxyethyl methacrylate (HEMA), and 2-hydroxypropyl methacrylate (HPMA) were distilled under reduced pressure prior to use. Azobisisobutyronitrile (AIBN) was recrystallized in methanol and dried under vacuum.

Copolymerization

Predetermined amounts of TBTM, (hydroxy)alkyl methacrylate, AIBN, and the solvent (toluene or tetrahydrofuran) were charged into a polymeriza-

* Present address: Industrial Tape Division, 3M Research Center, St. Paul, Minnesota 55144.

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 26, 595–599 (1988)
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TABLE I
Copolymerization of Tributyltin Methacrylate (M_1) with Hydroxyalkyl Methacrylate (M_2)

Polymer code	Mole fraction of M_1 in Feed (F_1)	Percent of tin in copolymer	Mole fraction of M_1 in copolymer (f_1)
	TBTM (M_1)–HPMA (M_2)		
HPT_2	0.22	8.83	0.13
HPT_3	0.30	13.09	0.21
HPT_4	0.39	16.40	0.29
HPT_5	0.63	23.17	0.51
	TBTM (M_1)–HEMA (M_2)		
HET_1	0.085	3.10	0.04
HET_2	0.20	7.25	0.09
HET_3	0.27	8.8	0.12
HET_4	0.36	12.08	0.18
HET_5	0.60	20.75	0.40

Note: Polymerization conditions: catalyst; AIBN, 0.1 % w/v; temperature, 55 ± 0.1°C.

TABLE II
Copolymerization of Tributyltin Methacrylate (M_1) with Alkyl Methacrylates (M_2)

Polymer code	Mole fraction of M_1 in feed (F)	Percent of tin copolymer	Mole fraction of M_1 in copolymer (f)
	TBTM (M_1)–CMA (M_2)		
$CHTM_1$	0.12	7.71	0.13
$CHTM_2$	0.26	11.98	0.21
$CHTM_3$	0.35	16.36	0.33
$CHTM_4$	0.45	18.80	0.40
$CHTM_5$	0.68	23.79	0.57
	TBTM (M_1)–EEMA (M_2)		
$EETM_1$	0.11	8.82	0.14
$EETM_2$	0.25	16.08	0.30
$EETM_3$	0.34	17.20	0.33
$EETM_4$	0.43	21.71	0.48
$EETM_5$	0.80	24.37	0.58
	TBTM (M_1)–EMA (M_2)		
ETM_1	0.087	10.25	0.13
ETM_2	0.020	15.79	0.23
ETM_3	0.363	20.06	0.34
ETM_4	0.612	25.35	0.55

Note: Polymerization conditions: catalyst; AIBN, 0.1% w/v; temperature, 55 ± 0.1°C.

TABLE III
Monomer Reactivity Ratios of TBTM with Alkyl Methacrylates

M_1	M_2	r_1	r_2	r_1r_2
TBTM	CHMA	0.41	0.85	0.35
TBTM	EEMA	0.40	0.65	0.26
TBTM	EMA	0.25	0.59	0.15
TBTM	HEMA	0.39	2.45	0.96
TBTM	HPMA	0.65	1.77	1.15

tion tube, followed by degassing (three freeze-thaw-pump cycles). The tubes were sealed, and the polymerizations were conducted at 55°C. After the desired reaction intervals, the resulting polymer solutions were precipitated into a large excess of *n*-hexane for the TBTM–hydroxylalkyl methacrylate series and methanol-water (9 : 1) for the alkyl methacrylate–TBTM series. The polymers were further purified by repeated dissolution and reprecipitated. Overall conversion was calculated from the weight of polymer obtained from a known amount of reaction mixture. The tin content of the copolymers was determined by the method of Gilman and Rosenberg.[6] The reaction conditions are summarized in Tables I and II.

RESULTS AND DISCUSSION

The feed ratios of monomers and the resultant copolymer compositions as determined from tin analyses were used to calculate reactivity ratios. The Kelen–Tüdös method was employed to determine the monomer reactivity ratios (Table III). Figures 1 and 2 show the copolymer composition as determined from elemental analysis as a function of feed composition for various copolymer systems. The copolymerization curves are based on the experimentally determined reactivity ratios. TBTM–HPMA copolymers contained a greater proportion of HPMA than the feed. This phenomenon is more

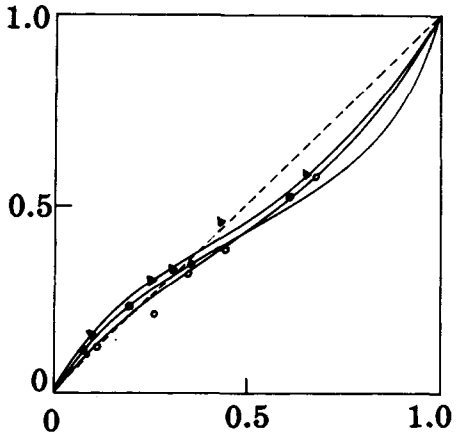

Fig. 1. Copolymer composition as a function of feed composition for the copolymerization of TBTM with CMA (○), TBTM with EEMA (●), and TBTM with EEA (▲).

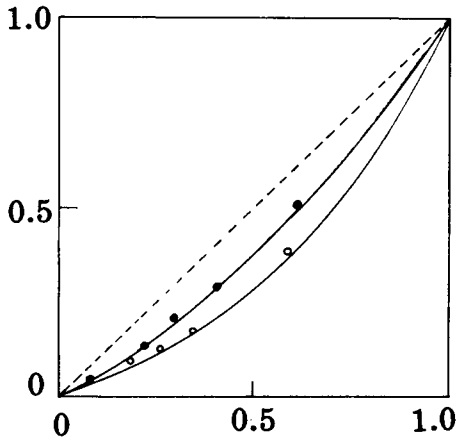

Fig. 2. Copolymer composition as a function of feed composition for the copolymerization of TBTM with HEMA (○) and TBTM with HPMA (●).

pronounced for the TBTM–HEMA copolymers. The high reactivity of functional monomers as compared with TBTM may be attributed to the association of the former monomers around propagating chains in THF medium. On the other hand all TBTM–alkyl methacrylate copolymers possess a definite alternating tendency. Since r_1 and r_2 are less than unity, the theoretical curve, F_1 versus f_1 intersects the line representing $f_1 = F_1$. At these intersection points the copolymers have the same composition as the monomer feed mixtures, and the polymeric products of constant composition are formed throughout the copolymerization reactions. In our study all the monomers are methacrylates, differing in their ester groups. Since the inductive effect of such groups can be neglected, only steric effects may influence the reactivities of the different monomers towards the TBTM polymer radical. The inverse of reactivity ratios $1/r_1 = k_{12}/k_{11}$ gives the order of magnitude of the reactivity of the alkyl methacrylate monomers towards the same reference polymer radical. A perusal of the data shows that $1/r_1$ remains nearly constant (within experimental error). It may, therefore, be concluded that the chain length of the ester groups of the three methacrylates has a minimal effect on the collision factor.

BIOTOXICITY

Table IV lists inhibition data for the TBTM-HEMA and TBTM-HPMA copolymers. Tests have been done in triplicate. The toxicities of these copolymers occur from the rate of hydrolysis of tin moities, which may be dependent on various factors, namely copolymer sequence distribution, cotacticity, and steric and polar nature of the comonomers. In our studies the toxin leaching rate was estimated from the annular inhibition zone, assuming the particle size of all the copolymers are nearly the same within experimental conditions.

TABLE IV
Test Microorganisms Inhibition by Copolymers

Polymer code	Percent of TBTM in copolymer	Weight of copolymer used (mg)	Size of zone (cm)	
			Sarcin lutea	Pseudomonas acruginosa
HET_1	9.78	5	1.51 ± 0.27	0.68 ± 0.50
HET_4	38.10	5	1.42 ± 0.32	0.70 ± 0.10
HPT_1	7.57	5	2.84 ± 0.48	0.75 ± 0.57
HPT_4	51.73	5	1.61 ± 0.18	0.93 ± 0.15

It may be concluded from the data in Table IV that the copolymer composition has an insignificant effect on the size of the inhibition zone.

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Received August 28, 1986
Accepted August 29, 1987