

Grafting. IV. Graft Tercopolymers as Antifouling Resin

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SYNOPSIS

A graft tercopolymer CLR-*g*-(MMA-TBTMA) based on chlorinated rubber as the backbone and binary copolymer of methyl methacrylate and tributyltin methacrylate as grafted chains has been synthesized. This graft copolymer has been used for the formulation of controlled-release antifouling paints, and leaching rate behavior of toxin from such paints has been studied. The data have been compared with those obtained using controlled-release antifouling paint based on linear chain copolymer of methyl methacrylate and tributyltin methacrylate. The paint based on grafted copolymer is characterized by having a lower leaching rate and reduced time for attainment of steady-state leaching. Raft exposure studies indicate longer antifouling life compared to that of linear chain copolymer-based paint both having the same dry paint film thickness.

INTRODUCTION

The importance of organotin-containing polymers for application in marine paint formulation is based on the appreciably large spectrum of the "kill" of selective organotin moieties and the self-polishing characteristics of the paint. Montermoso et al.¹ first reported the preparation of homopolymer and copolymers of tributyl methacrylate with an aim to produce thermally stable and chemically resistant materials. However, these polymers turned out to be susceptible to controlled hydrolysis and thus began a new era on the development of antifouling controlled-release polymers. Since then, a number of polymers containing releasable organotin toxin has been prepared and homopolymerization and copolymerization of tributyltin methacrylate have been studied in detail.²⁻⁶ It has been recently reported⁷ that a release rate of about 0.25–0.50 $\mu\text{g}/\text{cm}^2/\text{day}$ of tributyltin oxide (TBTO) is sufficient to prevent fouling contrary to about 1 $\mu\text{g}/\text{cm}^2/\text{day}$ reported earlier.⁸ It was established⁷ that about 30 mol % of tributyltin methacrylate in copolymer with methyl methacrylate is necessary to have sufficient antifouling activity.

There is no report, as far as our knowledge of the literature, on the use of graft copolymers containing TBTO as antifouling material. These graft branched polymers are expected to offer interesting possibilities because the leaching characteristics of TBTO from such copolymers may be different from linear chain homopolymers in that a branched molecule is normally more coiled (compact) and, hence, release of toxin may be more controlled.

In this paper, the synthesis of graft tercopolymer, viz. chlorinated rubber-*g*-methyl methacrylate-*co*-tributyl tin methacrylate [CLR-*g*-(MMA-TBTMA)], and its characterization and release rate of toxin (tributyl tin oxide) from the polymer are reported. Preliminary reports on the behavior of a few coating compositions based on the graft tercopolymer are also reported.

EXPERIMENTAL

Synthesis of Graft Tercopolymer of CLR-*g*-(methyl methacrylate methacrylic acid)

Chlorinated rubber (65% chlorine, Rishiroop Polymers, India) was purified by a solution-precipitation technique using benzene and methanol. The polymer was dried at 50°C under reduced pressure. Methyl methacrylate (MMA) was purified by the usual method. Methacrylic acid was purified by repeated

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crystallization in bulk at $13.5 - 0.05^{\circ}\text{C}$, followed by distillation under reduced pressure of N_2 using a column packed with Cu foils. Both the monomers were purified just before use. Partially thiolated CLR was prepared by bubbling H_2S into a suspension of chlorinated rubber in 5% KOH solution of alcohol.⁹ The light creamish CLR changed to an ash-colored powder. The thiolated polymer was processed and stored under an atmosphere of oxygen-free nitrogen. The thiol equivalent of the polymer was determined by the method of Doly et al.¹⁰ The method of grafting has been reported earlier,¹¹ and the polymerization was continued for 2 h. The graft tercopolymer was precipitated in aqueous methanol (10/90 v/v). The polymer was redissolved in tetrahydrofuran and precipitated in aqueous methanol and then dried at 50°C under reduced pressure. The composition of the graft copolymer was ascertained from chlorine and carboxylic acid content.

Esterification of Graft Copolymer

A stoichiometric amount of TBTO in toluene was taken in a resin kettle with facilities for stirring and distillation. The solution is warmed to 60°C , and the graft copolymer is added portionwise while stirring the mixture. The temperature is slowly increased to about 75°C during the addition of the graft acid-ester copolymer. The water formed during reaction was removed by distillation under slightly reduced pressure. The progress of the reaction was monitored by estimation of free carboxylic acid groups as well as by free TBTO in isopropanol. At the end of the reaction, a clear homogeneous solution was obtained having a polymer content of about 20% by weight.

Paint Formulation and Determination of Leaching Rates

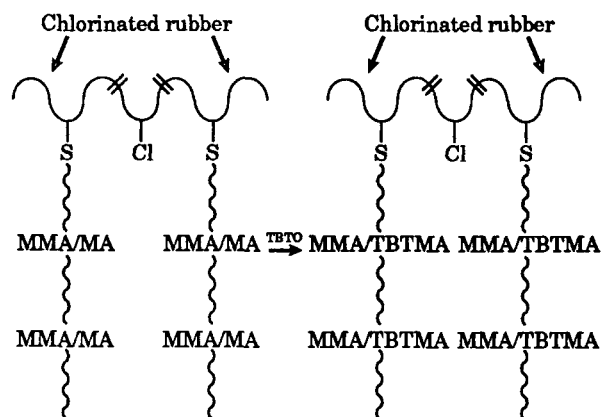
Resin solution along with appropriate amounts of chlorinated paraffin/DOP (plasticizer), red iron oxide, zinc oxide, and Al-stearate suspending agent was made into a homogeneous mix of paintable consistency by ball milling for 12 h. Glass panels of $12.5 \times 5 \times 0.2$ cm dimension were degreased and then painted on both sides with the paint to a dry film thickness of 100 ± 10 microns. Panels for raft assessment were of Perspex of $21.5 \times 15 \times 0.4$ cm dimension. Leaching rates were determined by the method reported earlier.⁷

RESULTS AND DISCUSSION

The mechanism of graft copolymerization of MMA on halogen-containing polymers via thiolation has

been proposed and verified earlier.⁹ It was found that MMA was very efficiently grafted on PVC as well as on CLR chains through a polythiol-DMSO reaction, whereas methacrylic acid was sluggish in forming grafted chains. However, a mixture of monomers containing MMA should respond favorably as it should form the first initiating radical and subsequent propagation should proceed depending on the reactivity ratios of the MMA-methacrylic acid monomer pair. A few runs indicated the success of ternary grafting.¹¹ The polymer obtained by the grafting reaction was found to consist of graft copolymers only, as evident from fractional chemical analysis and precipitation and selective solvent extraction with the CCl_4 - CH_3OH mixture.¹²

The general structure of the graft copolymer can be depicted as



This is an oversimplified pictorial representation since chlorinated rubber is known to have a complex chain structure having cyclic components also along the chain. Table I shows the composition of the graft tercopolymer *vis-à-vis* the copolymerization composition. The feed composition was based on the reactivity ratios¹¹ of the MMA-MA comonomer system measured in the presence of chlorinated rubber and polyvinyl chloride and on that the TBTM-containing resin should contain about 60% TBTM component (corresponding to about 33 mol % of TBTM in the MMA-TBTM random binary copolymer) to have appreciable toxin-release characteristics. A typical paint composition was made with this graft copolymer resin and other neutral pigments and plasticizer, and leaching characteristics are shown in Figure 1. The slow release rate of tributyl tin oxide/hydroxide has been plotted against the days of exposure in sea water under laboratory conditions. The release rate behavior of toxin from an equivalent point but containing linear MMA-TBTM copolymer is also presented for comparison.

Table I Compositions of Graft-Copolymerization Mixture *Vis-à-Vis* Graft Copolymer Obtained Using Polymeric Thiol-DMSO Initiator System at 60°C in Cyclohexanone

Copolymerization composition	
Chlorinated rubber	8.84%
MMA	40.34%
MA	42.92%
DMSO	7.90%
Graft copolymer composition [(CLR- <i>g</i> -(MMA-MA))]	
Chlorinated rubber	32.6%
PMMA	41.8%
PMA	25.6%

The superimposition brings out a few distinguishing features of the grafted copolymer. The two compositions were made nearly identical except that one is based on a linear copolymer of MMA-TBTM and the other on CLR-*g*-(MMA-TBTM), both containing about 60% TBTM. The leaching rates as depicted in Figure 1 show that for the graft copolymer it is, in general, lower than that of the linear

copolymer. The solvents in the two paint formulations are also the same, and lower leaching rates can be best explained on the basis of the more compact nature of the grafted chains. A second difference is the attainment of a steady state of leaching. Whereas in the case of linear copolymers it takes about 60 days to attain the steady state, in the case of graft copolymer, the same is attained in about 20 days time. The linear copolymer being less compact allows a deeper penetration and extended wetting by sea water. The subsequent attained steady state therefore is delayed. This is also probably the reason of higher leaching rates for the paint containing linear polymer.

As is evident, a steady-state leaching rate of about $0.25 \mu\text{g}/\text{cm}^2/\text{day}$ is obtained with graft copolymer-based paint. This leaching rate is generally thought of as lower than the critical leaching rate necessary to prevent fouling, as a minimum of about $0.40 \mu\text{g}/\text{cm}^2/\text{day}$ is considered the threshold limit. Table II shows the results of the raft exposure study extended for 30 months. As is evident, the exposure panels with about 200μ -thick dry paint film could remain foul-free for about 30 months.

It was established earlier⁷ that for linear chain toxic copolymer (MMA-TBTM)-based paint, an antifouling life of about 10 months for 100μ -thick

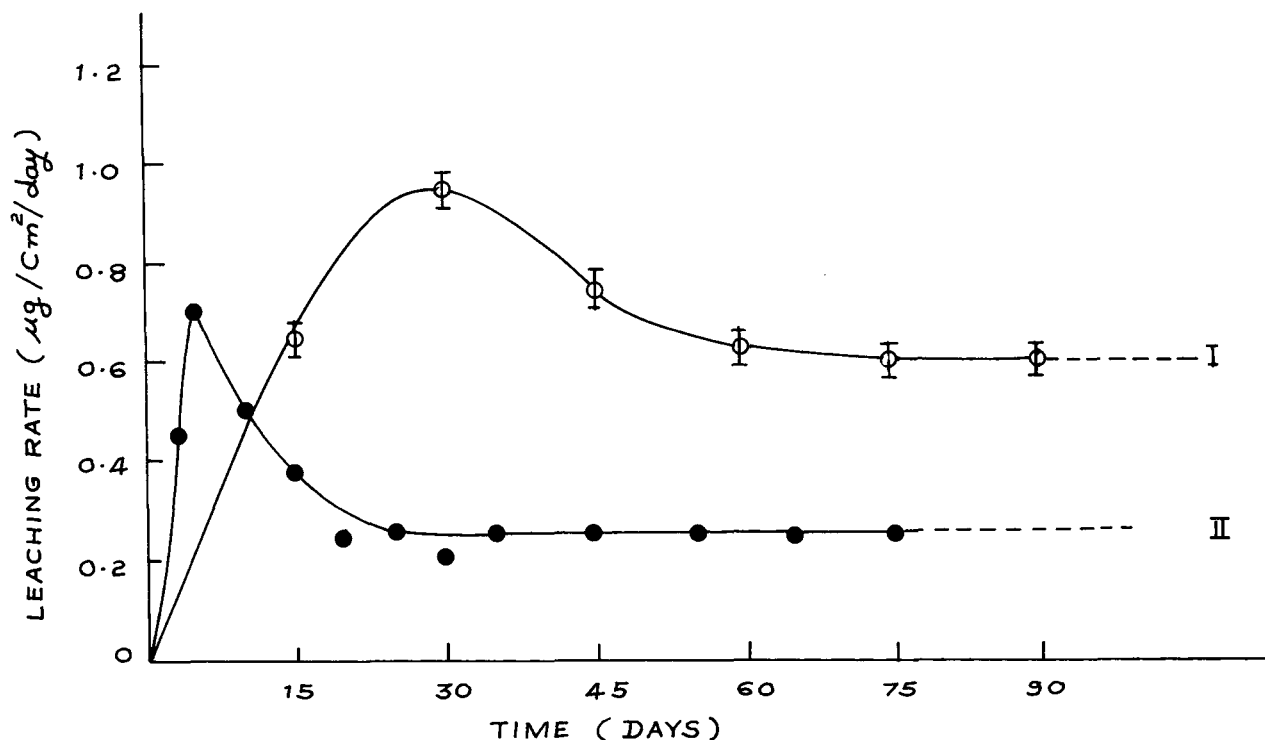


Figure 1 Leaching rate behavior of paints based on toxic linear copolymer (I) and toxic graft copolymer (II). Paint film thickness = $100 \pm 10 \mu$.

Table II Raft Exposure Study of Antifouling Paint Compositions Based on Toxic MMA-TBTMA Linear Copolymer and Toxic CLR-g-(MMA-TBTMA) Graft Copolymer (Paint Film Thickness = $200 \pm 20 \mu$)

No.	Composition	Period of Exposure (in months)				
		6	12	18	24	30
1.	Control	F	F	F	F	F
2.	Linear copolymer + plasticizer (DOP) + neutral pigments	NF	NF	NF	F	F
3.	Graft copolymer resin + plasticizer (DOP) + neutral pigments	NF	NF	NF	NF	NF

F = fouling; NF = no fouling.

paint film is achievable. In contrast, the present composition based on graft copolymer offers a distinct advantage in that much lower thickness is necessary to afford comparable antifouling protection (about $65 \mu/10$ months). The graft exposure results for the paint based on MMA + TBTM linear copolymer are also included in Table II for comparison.

CONCLUSION

It is thus concluded that an antifouling paint based on a toxic graft copolymer has distinct advantages over paints based on linear copolymers. Having the same toxin content, a paint based on graft copolymers offers an extended antifouling life due to a lower leaching rate presumably because of compactness of graft copolymer chains (branched). An antifouling life of about 10 months is achieved with a coating thickness of about 65μ compared to 100μ for linear copolymer chains. The steady-state leaching rate of toxin is reached in a much shorter time in a graft copolymer-based paint than in the case of a paint based on linear copolymer. The existence of a steady-state leaching rate enables one to formulate paints with a predicted life based on thickness only.

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Received December 6, 1990

Accepted December 20, 1990