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Photograft Copolymerization of Methyl Methacrylate and Natural Rubber Using Quinoline-Bromine C.T. Complex as Photoinitiator in Benzene Solution*

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ABSTRACT

Photografting of poly(methyl methacrylate), PMMA chains on natural rubber (NR) chain backbones was studied in benzene solution using quinoline-bromine (Q-Br₂) charge transfer complex as photoinitiator and MMA as monomer at 35°C in visible light. Analysis of overall products for determination of grafting efficiencies was done following a method of selective extraction of only the free rubber fraction by benzene-petroleum ether mixtures followed by separation of the NR-PMMA graft copolymer from free PMMA in the residue (taken in benzene solution) by fractional precipitation with methanol. High grafting efficiencies in the range of 75-95% were easily and generally obtained. Effects of variation of concentrations of initiator, rubber, and monomer on grafting efficiencies were examined and reported. Prior photodegradation of the rubber resulted in substantial lowering in grafting efficiencies. Overall mechanism of graft copolymerization has been discussed.

*Presented at the International Rubber Conference held at the Indian Institute of Technology, Kharagpur, West Bengal, India, in December 1980.

INTRODUCTION

It has been reported from our laboratory that halogens and a variety of charge transfer (C.T.) complexes of halogens, particularly those of bromine, act as good photoinitiators of vinyl polymerization [1-7]. Among the C.T. complex initiators studied, quinoline-bromine ($Q-Br_2$) complex has been used for broad-based kinetic and mechanistic investigations on vinyl photopolymerization using methyl methacrylate (MMA) as the monomer [5, 6]. This complex and other bromine complexes of this nature have also been found to be good reagents to effect exclusive additive bromination at natural rubber unsaturations [8].

In this paper we report results of photopolymerization of MMA in the presence of natural rubber, NR (1,4-cis-polyisoprene), in benzene solution employing quinoline-bromine ($Q-Br_2$) C.T. complex as photoinitiator leading to production of NR-PMMA graft copolymer.

EXPERIMENTAL

Materials

A fresh sample of NR pale crepe was purified first by acetone extraction and then by precipitation with excess methanol (containing about 0.5% dissolved SO_2 in order to destroy any peroxide present) from benzene solution. The purified rubber was collected, profusely washed with pure methanol, dried in vacuum at $50^\circ C$, and then dissolved in benzene under purified nitrogen to about 3% concentration.

Monomer MMA was purified by the usual procedures. Quinoline-bromine ($Q-Br_2$) complex, the photoinitiator, was prepared according to a procedure given before [5].

Photograft Copolymerization

A known volume of MMA was added to a known volume of the purified rubber solution in benzene under flowing nitrogen in a clear borosilicate test tube and finally a known quantity of the $Q-Br_2$ complex in benzene solution was added to the mixture. Polymerization was then carried out in a nitrogen atmosphere at $35 \pm 2^\circ C$ by placing the test tube close to a 40-W tube lamp for a specified time period.

From the gross polymerization product, isolated by precipitation with excess methanol and drying in vacuum, the NR-PMMA graft copolymer fraction was separated from the free (unreacted) NR and free PMMA fractions by selective extraction of free NR by benzene-petroleum ether mixture in appropriate quantities followed by dissolving the residue in benzene and then fractional precipitation of NR-PMMA

graft copolymer using methanol as the nonsolvent according to an established procedure [9, 10]. Free PMMA was then precipitated from the solution phase by excess methanol. The respective polymer fractions were then collected and dried in vacuum at 50°C.

RESULTS

Results showing grafting efficiency E_R (with respect to rubber) and E_M (with respect to PMMA) are presented in Tables 1-3. E_R and E_M represent the percentage of total rubber hydrocarbon and that of total PMMA appearing in the graft copolymer fraction, respectively.

The effects of variation of time of polymerization, concentration of the initiator ($Q-Br_2$), monomer concentration, and rubber content on E_R and E_M were examined. The effect of prior photodegradation of rubber on the grafting efficiencies was also studied.

Effect of Variation of Time

Grafting efficiencies of a fairly high to very high order (70-99%) were observed in general with undegraded rubber. With increasing time of polymerization, E_R value shows an upward trend and E_M value exhibits just the opposite trend, quite expectedly (Table 1).

Effect of Variation of [$Q-Br_2$]

At low initiator concentrations (< 0.008 mol/L) for a given time (5 h), close to 100% E_M value was observed, but E_R values were much lower (40-70%). With increasing initiator concentrations, E_R values improve significantly while E_M values followed a decreasing trend (Table 1).

Effect of Prior Photodegradation of Rubber

Photodegradation of rubber in benzene solution was done under nitrogen atmosphere in direct sunlight leading to reduction in intrinsic viscosity in benzene at 30°C from 4.8 to 0.52 dL/g, and a consequent lowering in % unsaturation from 99.82 to 91.80. With the degraded rubber, grafting efficiencies were of a substantially lower order in general (Table 1) and increasing initiator concentration produced increasing trends in both E_R and E_M .

TABLE 1. Graft Copolymerization of Rubber and Methyl Methacrylate^a

System	Wt. of rubber (g)	Initiator concentration (mol/L)	Time of polymerization (h)	Gross polymer (g)	Grafting efficiency (%)	
					E _R	E _M
A ^b	0.1617	0.0172	2	0.5311	79.15	86.13
			3	0.6691	81.32	81.84
			4	0.8436	80.51	76.12
			4 $\frac{1}{2}$	0.8967	83.67	78.73
			5	0.9145	92.05	74.14
B ^b	0.1860	0.0043	5	0.3444	43.51	98.68
				0.5487	72.43	99.75
				0.7345	85.78	80.23
				0.8929	86.54	75.01
				0.8724	96.86	74.51
C ^c	0.1890	0.0043	5	0.3074	19.04	56.67
				0.4409	28.14	58.41
				0.5208	28.51	56.57
				0.7118	39.36	63.92
				0.8900	46.66	71.38

^aBenzene (distilled), 6 mL; MMA, 3 mL; tube light (35°C), initiator, Q-Br₂.

^bUndegraded natural rubber: % unsaturation = 99.82; $[\eta] = 4.8$ dL/g.

^cDegraded natural rubber: % unsaturation = 91.80; $[\eta] = 0.5225$ dL/g.

Effect of Variation of Monomer Content

Low monomer concentrations produced close to 100% E_M value and also very high E_R value at the same time. Under this condition the graft copolymer appeared to be somewhat cross-linked and swelled heavily in benzene. At higher monomer concentrations the graft copolymer was soluble in benzene and E_R values observed were close to 90% while E_M values were between 65-75% (Table 2).

TABLE 2. Effect of Variation of Monomer Concentration on Graft Copolymerization^a

System	Wt. of rubber (g)	Volume of MMA (mL)	Time of polymerization (h)	Gross polymer (g)	Grafting efficiency (%)	
					E _R	E _M
A	0.1576	0.5	5	0.2477	79.60 ^b	99.50
		1.0		0.3543	86.04 ^b	99.84
		1.5		0.4518	88.89 ^b	99.89
		2.0		0.4598	89.02	67.43
		2.5		0.5554	91.97	69.22
		3.0		0.9042	92.05	74.14

^aBenzene (distilled), 6 mL; tube light (35°C); initiator (Q-Br₂), 0.0172 mol/L. Undegraded natural rubber: % unsaturation = 99.82; $[\eta] = 4.8$ dL/g. Total volume (rubber solution + MMA): 9 mL.

^bGrafted rubber did not dissolve completely but swelled heavily in benzene.

Effect of Variation of Rubber Content

Variation of rubber content produced small changes in grafting efficiencies as shown in Table 3, increasing rubber content producing an increasing trend in E_M in general.

All the separated PMMA fractions gave negative tests to the sensitive colorimetric test [11] for the presence of natural rubber hydrocarbon in them, while the test was positive for graft copolymer fractions. Overall loss in materials was within 3-5% in all the experiments.

Mechanism

The Q-Br₂ complex is reported to form further complexes of an unstable nature with vinyl monomers [6]. With MMA, bromine addition at monomer unsaturation via this complexation reaction is not a favored reaction and polymerization is initiated radically in preference, the rate of polymerization being much faster in light than in the dark [5, 6]. When used in large excess, Q-Br₂ complex acts as a good and efficient brominating reagent at natural rubber unsaturation (additive bromination) [8]. It is likely that the addition reaction

TABLE 3. Effect of Variation of Rubber Concentration on Graft Copolymerization^a

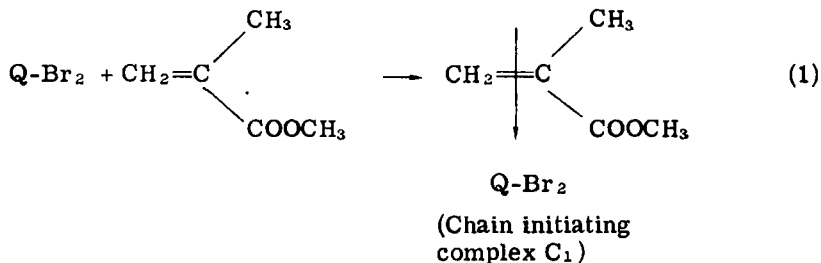
System	Wt. of rubber (g)	Volume of MMA (mL)	Time of polymerization (h)	Gross polymer (g)	Grafting efficiency (%)	
					E _R	E _M
A	0.0372	3	5	0.7615	77.55	87.49
	0.0744			0.8262	80.24	91.86
	0.1116			0.8427	87.85	84.06
	0.1488			0.8602	89.03	74.33
	0.1617			0.9145	83.73	74.14

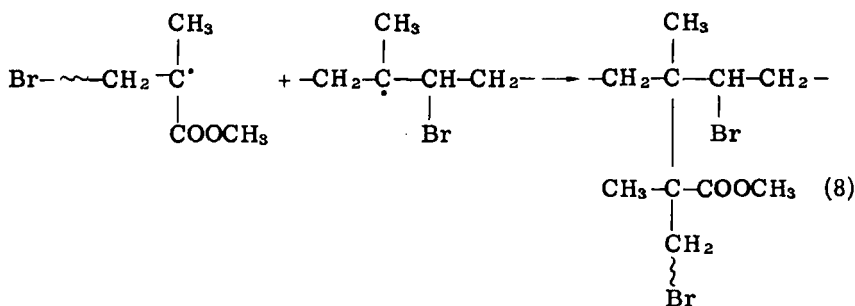
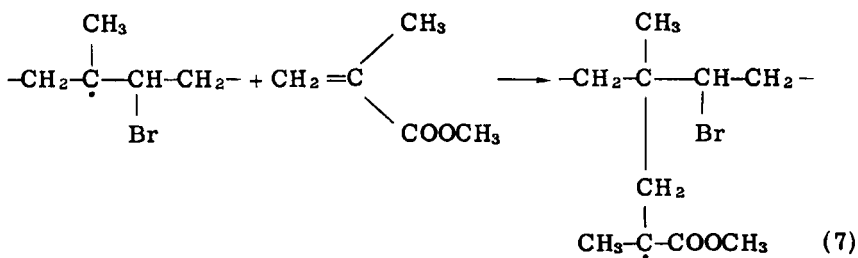
^aBenzene (distilled), 6 mL; tube light (35°C); initiator (Q-Br₂), 0.0172 mol/L. Undegraded natural rubber: % unsaturation = 99.82; [η] = 4.8 dL/g. Total volume (rubber solution + MMA): 9 mL.

also proceeds radically via complexation between Q-Br₂ complex and unsaturation points of the isoprene units in rubber molecules. Brominated rubber was also observed to be unstable, particularly at high temperature and on photoactivation, slowly evolving bromine and perhaps some hydrogen bromide.

Thus, when a mixture of natural rubber hydrocarbon (in benzene solution), MMA, and Q-Br₂ (benzene solution) are mixed in the given sequence and then the system is exposed to visible light under an inert atmosphere, the following sequence of reactions are considered to take place:

Complexation:



Graft copolymer formation:

DISCUSSION

In the sequence of reactions given above, graft copolymer formation takes place according to reactions given in Eqs. (7) and (8). Kinetic studies indicated that in the Q-Br_2 complex initiated photopolymerization of MMA, particularly in the presence of solvents or additives, bimolecular termination involving PMMA chain radicals practically recedes to insignificance and termination by degradative chain transfer involving solvent/additive-modified initiating complexes and the propagating radicals assumes prominence [6]; for $[\text{Q-Br}_2] > 0.003 \text{ mol/L}$ and benzene content $\geq 25\% \text{ (v/v)}$, R_p (rate of polymerization) becomes practically independent of $[\text{Q-Br}_2]$ [6]. Primary radical termination is also likely to be of some significance, and PMMA obtained under this condition are considered to be telechelic in nature with bromine endgroups at each end of the linear chains, one incorporated during initiation and the other during termination by the degradative effect or by primary (bromine) radicals.

Very high grafting efficiencies (E_R and E_M) in the natural rubber-MMA-(Q-Br_2) photosystem in benzene solution indicates that the initiating complex C_2 is more consequential for chain initiation, particularly at low concentrations of the initiator and monomer, the

consequential chain initiating radical being the bromo isoprenyl radical ($-\text{CH}_2-\text{C}(\text{CH}_3)-\text{CHBr}-\text{CH}_2-$). Besides the reactions given above, chain transfer between PMMA chain radicals and rubber chain molecules (unmodified or modified through complexation as in reaction steps 2) and 4a), generating fresh radical sites on the rubber chains may also partly account for the grafting process. For the polymer grafted-on growing chains, termination is most likely to take place by degradative transfer processes involving solvent-modified chain initiating complexes C_1 and C_2 and perhaps also by primary bromine radicals, and bimolecular termination is likely to be practically insignificant [6]. Photodegradation of rubber results in lowering in the unsaturation content through cut down of chain lengths and also probably through cyclization to a certain extent, leading to lower grafting efficiencies.

With catalytic concentrations of the $\text{Q}-\text{Br}_2$ complex in the present experiments (< 3.5 mol% of the isoprene units of rubber taken), loss in rubber unsaturation is considered very low or insignificant. Except for three experiments with low monomer content (Table 3), the separated polymer fractions were all soluble in benzene. This is in contrast to the fact that when natural rubber is significantly brominated additively, it becomes insoluble in benzene.

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