

FREE RADICAL COPOLYMERIZATION OF STYRENE AND SHELLAC - GLYCOL ESTER

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The benzoyl peroxide initiated copolymerization of styrene and shellac-glycol ester (SGE) was accomplished at 75°. Both styrene and SGE molecules participate in the reaction and the growing polymer chains of styrene and SGE couple to form a copolymer at all monomeric ratios. The monomer reactivity ratios of styrene (r_1) and SGE (r_2) as determined using integrated form of Mayo were found to be $r_1=0.37$ and $r_2=1.5$. With an increasing concentration of SGE in the binary mixture, the copolymer of increasing molecular weight ($M_n = 140756 - 211443$) were obtained. The copolymer is light brownish solid substance. It softens at 107-108° and decomposes at 150°. The copolymer obtained at high feed of SGE (90%) is highly tacky and film forming. It may be used as a sealant for gaskets.

Key words: Shellac-glycol ester, Esterification, Degradation.

Introduction

The innumerable uses of shellac has been proved its versatility and commercial potential. It is generally used in the preparation of polishes, metal foils, varnishes undercoats, medicinal pills, insulating cloth, gramophone records, sealing waxes, optical cements, radio valves, abrasive papers and cloth, cosmetics, dental composition bangles making. Even the remarkable versatility of shellac it requires some modifications to make it more useful in various industries. For the same shellac has been subjected to variety of chemical treatments in order to elucidate its constituents and modify to suit the needs of certain industries. It can be esterified [1-4] with poly alcohols like ethylene glycols, propylene glycol, glycerol in the presence of mineral acid. Shellac glycol ester (SGE) so prepared is a viscous material which produces flexible films and may be used in the preparation of thermoplastic films. Survey of the literature provides so many references [5-9] that shellac forms copolymers by treating with various vinyl monomers in aqueous and nonaqueous media. These copolymers have outstanding film forming properties. It has been also observed that shellac glycol ester, if heated in the presence of vinyl monomers like MMA, butyl acrylate, styrene etc. forms a highly tacky film forming material. This is the copolymer of shellac glycol ester and vinyl monomer. This requires a detailed study of such products and their commercial exploitation. This paper deals with the copolymerization of styrene and shellac-glycol ester using benzoyl peroxide as an initiator.

Experimental

Material. (1) Styrene (BDH) was purified before use. The fraction boiling at 147-150° was used. (2) Propylene

glycol (BDH), isopropyl alcohol (BDH) and HCl (Merck) were used without further purification. (3) Ethyl alcohol of commercial grade was doubly distilled before use. (4) Reagent grade benzoyl peroxide was twice recrystallized in chloroform. (5) Shellac glycol ester (SGE) [10] was prepared by esterifying the free carboxyl group of shellac with propylene glycol. Before doing esterification of shellac, it dewaxed by dipping it in cold ethyl alcohol for 24 hr. Shellac will get dissolved in cold alcohol. Dewaxed shellac was then separated by distilling off alcoholic solution of shellac. A four neck round-bottom flask was fitted with a stirrer, thermometer, condenser and separating funnel. A known quantity (50 g) of dewaxed shellac was transferred to the reaction flask containing propylene glycol (160 g). The contents of the reaction flask are stirred for 15 min, and then few drops of HCl are added to it. The contents are refluxed at 100-110° for 6-8 hr without further stirring. After required reaction time a viscous dark brown material is obtained. This is the shellac-glycol ester of density 1.03 at 30°.

Procedure of copolymerization. The copolymerization reactions (expt. 1-5) were carried out in sealed tubes. Known quantity of shellac glycol ester and styrene were transferred to the reaction tubes already containing benzoyl peroxide (0.005 g). The reaction tubes were then sealed by constriction and heated. After required reaction time (10 hr) the reaction tubes were cooled and then broken open. The resulting product was separated with toluene-methanol solvent precipitant system. The product thus obtained was found soluble in hot toluene, acetone, ethyl methyl ketone, ethyl acetate etc. It is light brownish solid substance which may be powdered on crushing and softens at 106-107°. The I.R. spectrum of the product was recorded to ascertain the

copolymer formation which is as follows:- 3500 - 3300 (m), 2900 (s), 1920 (w), 1700 (m), 1600 (m), 1480 (w), 1440 (m), 1280 (w), 1020 (w), 900 (w), 840 (w), 740 (m), 680 (m) cm^{-1} wave number. The viscosity of a dilute solution of copolymer prepared in hot toluene was measured at 30° using an Ostwald's type viscometer.

Besides this, a binary mixture of styrene (9 g) and SGE (171 g) was copolymerized at 130-140° for 10 hr in the presence of benzoyl peroxide (0.173) in a four neck round bottom flask fitted with condenser stirrer, thermometer and separating funnel. After required reaction time, the heating is stopped and the product was washed with distilled water and dried under vacuum.

The hydroxyl group of the product was determined by the procedure based on esterification with acetic anhydride-pyridine mixture [10].

Results and Discussion

Data regarding the copolymerization of styrene and shellac glycol ester (SGE) using benzoyl peroxide as initiator at 75° are shown in Tables 1 and 2.

The copolymers were characterized by elemental analysis, solubility, I.R. spectral studies intrinsic viscosity, softening point. The composition of the resulting product

TABLE 1. COPOLYMERIZATION OF SHELLAC - GLYCOL ESTER (SGE) AND STYRENE AT 75° USING BENZOYL PEROXIDE AS AN INITIATOR FOR TEN HOURS.

Expt. No.	SGE g	Styrene g	Yield g	Analysis % -OH group
1.	0.5	4.5	4.2	0.90
2.	0.9	4.1	3.7	1.55
3.	1.1	3.9	3.5	1.70
4.	1.3	3.7	3.1	1.90
5.	3.0	2.0	2.2	2.60
6.	3.7	1.3	0.5	3.10
7.	171.0	9.0	63	8.35
8.	5.0	-	1.0	9.20
9.	-	5.0	4.8	-

TABLE 2. SOME PHYSICAL PARAMETERS OF COPOLYMER OF SGE AND STYRENE.

Expt. No.	[η] dl/g	Mn	Probable no. of monomer units in copolymer (Pn)		Colour	Appearance	Softening range
			Styrene	SGE			
1.	0.47	140756	1227	12	Brown	Brittle solid	107-108
2.	0.48	144932	1170	22	Brown	Brittle solid	108
3.	0.51	157664	1231	28	Brown	Brittle solid	108
4.	0.54	170691	1361	32	Brown	Brittle solid	107
5.	0.63	211443	1928	70	Brown	Brittle solid	107
6.	0.38	104770	1007	-	White	Brittle solid	105
7.	0.42	-	-	-	Brown	Elastic rubbery	-

obtained by copolymerizing the binary mixture of styrene and shellac - glycol ester was carried out for -OH group. The five samples (Expt. 1-5) contain 0.9 - 2.6% -OH group (Table 1) whereas the prepared sample of shellac - glycol ester (SGE) contains 9.54% -OH group. SGE was heated with benzoyl peroxide in a sealed tube for 10 hr. The product obtained is an elastic rubbery material containing 9.2% -OH group. Presence of and difference in -OH group shows the attachment of SGE molecules to the growing polymer chain of poly-styrene. It evidences the formation of copolymer. Solubility is an important tool which play a significant role in the identification and ensuring the participation of both styrene and SGE in the copolymerization reaction. Polystyrene is soluble in cold toluene whereas SGE dissolves partially in toluene (cold or hot) but the solubility of its homopolymer further decreases. On the other hand the product gets dissolved in hot toluene and shellac itself is insoluble in toluene. Furthermore shellac and SGE are soluble in ethyl alcohol whereas the product does not dissolve in alcohol. The solubility behaviour supports the results of the analysis for -OH group and ensures that the product is a copolymer. The I.R. spectrum of product has been recorded and given elsewhere. In the spectra of the product, the absorption bands with maxima at about 2900, 1480, 1440, 1280, 1020 cm^{-1} are characteristics c-c bands whereas the absorption bands at 3500-3300, 1700, 1600 cm^{-1} indicate the presence of -OH, c=O and c=c (aromatic ring grouping) respectively.

In Fig. 1, yield (g) is plotted against styrene (g) in feed which indicates that in the binary mixture of styrene and SGE the rate of formation of copolymer increases with increasing concentration of styrene. From the estimation of the product samples for hydroxyl (-OH) group as summarized in Table 1, it is evident that the SGE molecules are incorporated in the copolymer chain.

At the early stages, the copolymerization of styrene and SGE gives an initial product which is virtually polystyrene. It is obvious from the results that both styrene

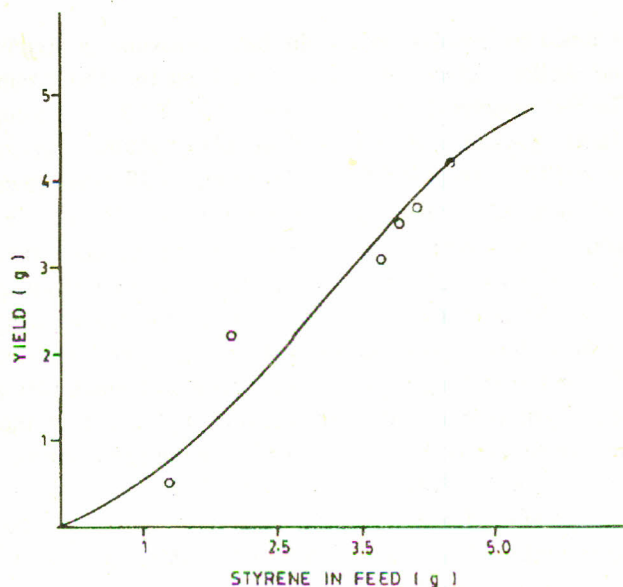


Fig. 1. Mayo and Lewis plot of r_2 against r_1 for the copolymerization of SGE (r_1) and styrene (r_2).

and SGE molecules participate in the reaction and the growing polymer chains of styrene and SGE couple to form a copolymer at all monomeric ratios. It is known that styrene on heating with or without catalyst may be readily polymerized. On the other hand SGE is an ester of shellac and propylene glycol which is obtained by the esterification of shellac by propylene glycol in the presence of mineral acid [10] as given elsewhere. Shellac ($M=1000$) is apparently a mixture of polyesters made up of various hydroxyl aliphatic and sesquiterpenic acid. It contains one free highly reactive acidic group, three ester linkages, five hydroxyl groups and a possibly free or potential aldehydes [12]. The carboxyl groups of shellac molecules reacts readily with propylene glycol resulting a viscous dark brown material which is the shellac-glycol ester and on prolong heating converts into an elastic rubber like material (dimer, trimer etc.) [13]. This shows that shellac glycol ester is like a prepolymer. On heating the binary mixture of styrene and SGE in the presence of benzoyl peroxide at the early stages, homo polymerization of styrene takes place and then the growing polymer chains of polystyrene and poly (SGE) colloids to form a copolymer. The addition of SGE molecules in the growing polymer chain of polystyrene, have changed all physical and chemical parameters of polystyrene and highly tacky brown material is resulted.

The monomer reactivity ratios of SGE (r_1) and styrene (r_2) were determined graphically by using integrated form of Mayo and Lewis equation [14]. In Fig. 2, r_2 values have been plotted against r_1 values. The values of r_1 and r_2 so obtained from this plot are respectively 0.37 and 1.5. Since

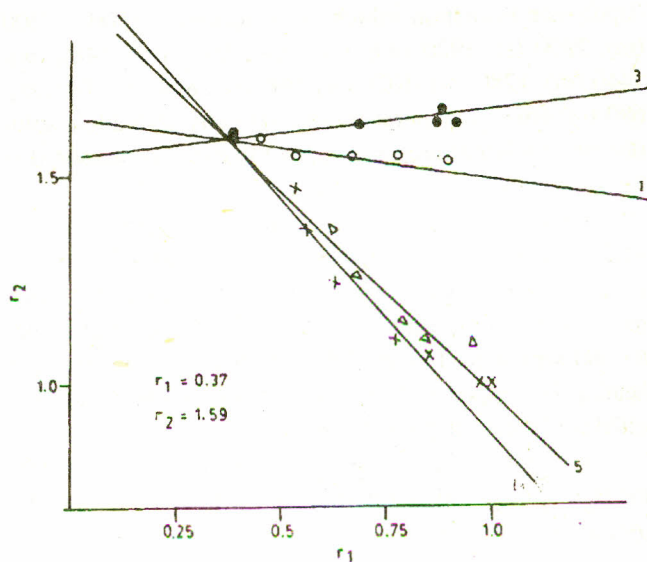


Fig. 2. A plot of yield (g) against styrene in feed (g) in the copolymerization of SGE and styrene.

one reactivity ratio is less than unity ($r_1 = 0.37$) and the other is greater than unity (1.59), the present copolymer system is nonazeotropic. As both r_1 and r_2 are greater than unity, both radicals prefer the same monomer i.e., styrene. This shows that styrene is more reactive than SGE. The rate of polymerization of styrene is certainly greater than the rate of polymerization of SGE.

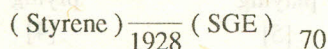
The simplest and most widely used method of determining molecular weights of long chain polymers is by the measurement of the viscosity of a dilute solution. The viscosity of dilute solutions of copolymer samples prepared in hot toluene were measured at $30 \pm 0.5^\circ$ using Ostwald type viscometer. The molecular weight of the copolymer samples were calculated by using the following relationship [16].

$$[\eta] = 0.923 \times 10^{-4} \bar{M}_n^{0.72}$$

where $[\eta]$ is the intrinsic viscosity in dl/g obtained by the intercept of the plot η_{sp}/C against C . Here η_{sp} is the specific viscosity and C is the concentration of dil solutions. The intrinsic viscosity of copolymer samples was found to be 0.47 - 0.63 dl/g which gives the molecular weight as 140756-211443. Keeping in view the chemical analysis and composition of monomers in copolymers, the degree of polymerization P_n have been calculated as shown in Table 2. These results indicate the major participation of styrene monomer units ($P_n = 1227-1928$) in the formation of copolymer as compared with SGE ($P_n = 12-70$). The results further envisage, that the addition of SGE molecules in the growing copolymer chain increases with increasing

concentration of SGE. Furthermore the change in intrinsic viscosities of copolymer samples might also be due to the presence of dye present in the starting material (dewaxed shellac). The dye rather acts as chain transfer agent. It lowers the molecular weight and degree of polymerization (Table 2).

Hence not only the styrene monomer units causes the increase in chain length but SGE molecules also affects in the formation of long chain copolymer. At a feed of 87.2 mole % styrene and 12.8% SGE, the copolymer of following type may be suggested.



This type of copolymer consists mostly styrene monomer units. At the highest feed of styrene expt. no.1 (Table 2) a mixture of polystyrene and styrene-Co-SGE is obtained which is also clear from estimation of -OH group (0.9%) and Pn values for styrene (1227) and SGE (12).

All copolymer samples first starts softening at 108-110° and then begins to decompose at 150°. On further heating, it converts into liquid and disappears at 250° with a peculiar smell of shellac leaving behind a dark brown horny material insoluble in alcohol. The transition state of the product from solid to liquid state is apparently gradual. The conversion of copolymer into liquid and its disappearance shows the degradation of copolymer into styrene dimer trimer etc. On the other hand polystyrene itself begins softening at 105° whereas shellac softens at 65° and melt at 77-90°. All these evidences show that shellac molecules (in the form of SGE) and styrene monomer have been incorporated in the copolymer chain.

In brief, shellac behaves like a thermoplastic when heated for a short period of time. If it is heated above its melting point ($\geq 150^\circ$) it undergoes polymerization giving an alcohol insoluble rubbery product. This polymerization proceeds through two distinct stages, a pre-gelation phase and a post-gelation phase [16]. Further shellac copolymerizes with both electron donating and electron accepting vinyl monomers in aqueous ammoniacal medium in the presence of redox pair such as ammonium peroxodisulfate and sodium bisulfite. This graft copolymer may be used for impregnating and coating purposes [8]. Shellac esterifies with propylene glycol through its carboxyl group and forms shellac glycol ester (SGE). On prolonged heating, it forms dimers, trimers etc. SGE may be copolymerized with styrene, At a low feed of SGE

(60%) it copolymerizes with styrene resulting in a copolymer brown in colour bearing density as 1.05. But at the high feed of SGE (90%) styrene and SGE form a very useful product (density 1.04) which is highly tacky and film forming. These films are resistant to water, Naptha, Kerosene oil and steam. Due to this property it may be used as a sealent compound for gaskets [17] (Table 2). From the estimation of the product for -OH group, it contains 8.35% -OH group whereas SGE itself, contains 9.5% -OH group. The high percentage of -OH group indicates the domination of SGE molecules in the copolymers chain.

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