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Soluble Itaconic Acid–Ethylene Glycol Polyesters

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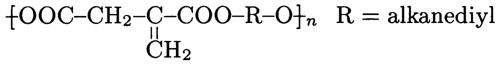
A method of obtaining soluble itaconic acid (IA)–ethylene glycol (EG) unsaturated polyesters was developed. The reaction between IA and EG was conducted under moderate vacuum (50—60 mmHg) at 120 °C and stopped by nearly 85% conversion to avoid crosslinking. No isomerization of itaconate to citraconate and/or mesaconate was observed. The residual double bond contained in the polyester resin showed to be highly reactive and promoted gelification after few days. Therefore copolymerization reactions of the resin with a variety of vinyl monomers proceed without radical initiator. The synthetic method was successfully applied to reactions of IA with other glycols.

Itaconic acid (IA) is an unsaturated dicarboxylic acid which is normally used in low percentages in formulations of commercial unsaturated polyesters in order to promote crosslinking reactions with styrene or other vinyl monomers.[1)] Synthesis of soluble polyesters of itaconic acid with glycols has not been reported so far (Fig. 1). This is due to the high reactivity of the vinyl double bond which is situated as a side group of the principal polyester chain and can therefore participate in crosslinking and gelification reactions and/or extensive isomerization under reaction conditions normally used for the preparation of polyesters.[2—4)]

Essentially, one can use itaconic acid based polyesters in applications where normally polyesters derived from maleic or fumaric acids are used as prepolymers to obtain resins of high technological interest. We have developed a procedure that permits the synthesis of soluble polyesters resins of IA with ethylene glycol (EG). These resins have been applied successfully as polymeric precursors in the preparation of ceramic oxides.[5)] Dimethyl itaconate and itaconoyl dichloride has also been used instead of itaconic acid for the synthesis of the polyester in our laboratories. On the other hand the possibility of using the monoester of itaconic acid with ethylene glycol, as the monomer, in polycondensation reactions is currently being evaluated.

Experimental

The technique of bulk polycondensation of IA with ethylene glycol under moderate vacuum (40—50 mmHg) has been employed in this work. When itaconic acid was directly polycondensed with ethylene glycol, *p*-toluenesulfonic acid (0.1% respect to IA) was used as catalyst. The reaction temperature was maintained at 120 °C in this case. However, when itaconoyl dichloride was condensed with EG, no catalyst was used and the reaction temperature was 60 °C. The transesterification reaction of dimethyl itaconate (DMI) with EG was also carried out. This was done in a similar manner to those of IA with the only difference that the polymerization reactions were performed at 100 °C.



$$\left[\!\!-\mathrm{OOC{-}CH_2{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}COO{-}R{-}O}-\!\!\right]_n \quad \mathrm{R = alkanediyl}$$

Fig. 1. Repeating unit of itaconic acid based polyesters.

In a typical preparation, 0.1 mol of IA was mixed with a slight excess (5%) of EG in the presence of hydroquinone (0.01%) as inhibitor. The polycondensation was carried out up to nearly 85% conversion which was estimated from the amount of water collected in a graduated cold trap.

Results and Discussion

Polycondensation Reactions. Direct polyesterifications of IA with EG under moderate vacuum at 120 °C results in obtaining soluble products only when the reaction conversion is kept below 85% as already mentioned. About two hours were necessary to reach this conversion under the above conditions. However, when the condensation reactions are conducted to higher conversions only crosslinked polymer is obtained. The transesterification of DMI with EG was carried out at slightly lower temperature (100 °C). It was observed that the polyesters obtained in this way were soluble products even though the reaction conversion was greater than 85%. The AI/EG and DMI/EG polyesters are soluble in acetone, chloroform, and tetrahydrofuran, less soluble in toluene and insoluble in water, benzene, and hydrocarbons. The polymers were purified by precipitating in water and then reprecipitating in a mixture of heptane–toluene (2 : 1). The polyesters kept at room temperature undergo crosslinking in solution or in bulk after 24 or 48 h. By adding an inhibitor, such as hydroquinone, and by storing the polyester samples at a temperature below −10 °C, the polymers remain soluble for a couple of weeks.

The values obtained for the number average molecular weights (M_n) of the AI/EG polyesters are between 500—700 as measured by gel permeation chromatography (GPC). When a catalyst such as *p*-toluenesulfonic acid is used for the polycondensation reaction, it is possible to obtain M_n of nearly 1200. Representative values of M_n of AI/EG based polyesters as function of reaction

Table 1. M_n Values of AI/EG Polyesters for Different Reaction Time[a)]

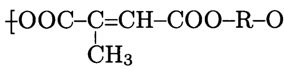
Sample	Reaction time (min)	M_n
1	30	570
2	45	920
3	75	1100
4	105	1140

a) Polyesterification carried out in the presence of *p*-toluenesulfonic acid.

time are shown in Table 1. The polydispersity in these systems is rather high and a broad molecular weight distribution is observed as is expected for this type of polymerization.

Isomerization. It is well known that when polyesters are prepared from unsaturated dicarboxylic acids with glycols, isomeirzation of these acids occurs. For example it has been observed that in polyesters prepared from maleic anhydride with different glycols, the polymeric chain contains both fumarate and maleate units. The proportion of these isomers was found to depend on the nature of the glycol used and temperature. It has also been established that when IA is polycondensed with glycols, considerable isomerization of this to citraconates and specially mesaconates occurs at high temperatures (180—200 °C).[3)] The ^{1}H NMR ($CDCl_3$) spectra of polyesters of the IA with EG obtained in this work show three bands in the region of vinyl protons, two of which ($\delta=5.8$ and 6.2) could correspond to the itaconic vinyl protons (in IA these are situated at $\delta=5.8$ and 6.1) and the third signal located at $\delta=6.7$ is in the region where mesaconic protons ($\delta=6.7$) normally appears. On the other hand, these spectra did not show signals corresponding to the methyl groups which should appear if isomerization of itaconate to citraconate and/or mesaconate take place (Fig. 2).

On this basis, we have discarded the existence of isomerization of itaconate under the reaction conditions used in this work. The origin of the signal at $\delta=6.4$ should be investigated further, but the presence of a signal at $\delta=4.4$ could indicate the participation of the double bond in addition reactions. The fact that the IA/EG resins have tendency to spontaneous crosslinking is an important aspect of this investigation. This phenomenon could be due to activation of residual double bonds which in these polyesters are situated as a lateral group, and therefore they could be more accessible in contrast to those of commercial maleic anhydride based polyesters or polyesters obtained from citraconic and mesaconic acids (which are isomers of IA), where this residual double bonds are located in the polymer main chain. This tendency to polymerization has been observed[6)] for higher esters of IA as compared with lower esters and in much extent with the parent acid. These oligomers could be considered as an special case of a higher ester of IA.



$$\left[\text{OOC-}\underset{\text{CH}_3}{\text{C}}\text{=CH-COO-R-O}\right]$$

Fig. 2. Citraconate (cis) or mesaconate (trans) units in polyester chain.

As was expected, polyesters obtained from condensation of citraconic and mesaconic acids with EG did not show any tendency for crosslinking although they were prepared under the same conditions of those used for IA.

Preliminary experiments showed that IA based polyesters copolymerizes readily with vinyl monomers such as styrene, methyl methacrylate, methyl acrylate, etc., in the absence of a radical initiator. From these reactions highly crosslinked copolymers are obtained. These non-initiated polymerization reactions, involving the residual vinyl bond in IA/EG polyester samples, clearly shows the strong activation of the double bond. Polycondensation of IA with other glycols such as diethylene glycol, triethylene glycol and 1,4-butanediol are currently under study.

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