

Cation Exchange Resins as Catalysts in the Preparation of Polyesters

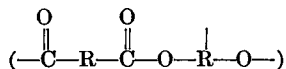
N. D. GHATGE, *National Chemical Laboratory, Poona, India*

Synopsis

Polyesters for use in preparation of flexible polyurethane foam were made by the use of C.N.S.L. cation exchange resin as catalyst in xylene medium. With 6% of the C.N.S.L. resin, the time needed to reach the lowest acid number (about 3.5) was 4 hr. For comparison, 2% of various cation exchange resins (C.N.S.L. resin, Zeo-Karb 215, Amberlite IR 20, and Amberlite IRC 50) were employed in xylene medium, to make the polyesters. The results indicated that in these polyesterification experiments, C.N.S.L. resin gave the lowest acid number in 14 hr.

INTRODUCTION

Polyesters are prepared by the self-condensation of ω -hydroxy acids or by the condensation of dibasic acids and glycols. Usually the structural unit of the polyester



determines the final nature of the polyester. Thus polyethylene adipate is a highly crystalline material, whereas polypropylene adipate is a viscous syrup. The difference between the two polyesters is due to the extra $-\text{CH}_2-$ group of propylene glycol. Similarly the presence of aromatic ring or the presence of unsaturation in the polyester chain, have their own effects on the final properties of the polyesters.

Substances which are used as catalysts for simple sterification are also used as catalysts for polyesterification. However catalysts are not quite often used in polyesterification, as their removal from polyesters by washing or by any other treatment presents many difficulties.

The process of manufacturing polyesters essentially consists of heating the ingredients at high temperature and at normal or reduced pressure, with or without a catalyst, for a period sufficient to give a product of the desired acid value. The present investigation relates to the preparation of the polyesters needed for synthesis of polyurethane foam by using cation exchange resins as catalyst.

Polyester for Flexible Foam

Polyesters used to produce polyurethane flexible foams¹ are reported to possess hydroxyl number in the range of 50–55, acid number of 1–2, and viscosities of 8,000–13,000 cpoise.

In Table I are given the conditions of time, temperature, and pressure used in preparing a polyester for foam preparation with the physical properties as reported above.

TABLE I
Time, Temperature, Pressure Required for Polyester Preparation

Heating period, hr.	Temperature, °C.	Pressure, mm. Hg
5	180–190	760
4	200–210	25–30
12	210–220	5

Thus in all 21 hr. are needed to prepare a polyester when no catalyst is used. It was therefore decided to shorten the time of polyesterification by employing a suitable catalyst.

Since the polyester needed for foam preparation must be free from traces of catalyst, it was decided to use a solid catalyst which is insoluble in the polyester medium during preparation period. One such catalyst, which was easily available, was C.N.S.L. cation exchange resin, a product of this laboratory.

Cheetham² and Spurlin³ first reported the use of cationic and anionic exchange resin as catalysts. These workers used cation exchange resins in presence of salts as catalysts, and it was assumed that the resins reacted first with the salt to liberate the acid, which ultimately catalyzed the reaction. Later results showed that cation exchange resins alone can be used as catalyst in esterification.⁴

EXPERIMENTAL

To a benzene or xylene solution of the glycols and the dibasic acids, in a three-necked flask fitted with a stirrer and a Dean and Stark apparatus, was

TABLE II
Polyester Formulation

Component	Amount
Dibasic acid I	1.5 moles
Dibasic acid II	1.5 moles
Glycol I	3.25 moles
Glycol II	0.25 moles
C.N.S.L. resin	2, 4, 6, or 10%
Benzene or xylene	—

added the requisite percentage of the cation exchange resin. The contents were refluxed till the lowest acid number was reached. The solvent was distilled off and the acid number, the hydroxyl number, and the viscosity determined.

C.N.S.L. cation exchange resin, a product of this laboratory, was used as catalyst in a polyester formulation as shown in Table II.

It was observed in early experiments that some glycol was lost from the polyester formulation in the azotropic removal of water. Hence identical sets of experiments were carried out, in which, in one set, all the glycol quantity was added initially to the formulation and the experiments carried out as mentioned (Table III). In the second set of experiments, half

TABLE III
Physical Properties of Polyesters Obtained with Initial
Addition of Entire Amount of Glycol

Solvent	Catalyst, %	Time, hr.	Acid number	Hydroxyl number	Viscosity, cpoise
Benzene	4	14	23.0	76.0	4200
	10	14	8.1	67.7	5400
Xylene	4	8	2.33	51.3	8200
	6	4	2.64	52.00	8000

TABLE IV
Physical Properties of Polyesters Obtained with
Addition of the Glycol in Two Equal Portions

Solvent	Catalyst, %	Time, hr.	Acid number	Hydroxyl number	Viscosity, cpoise
Benzene	4	14	20.1	77.5	4100
	10	14	11.0	74.2	5000
Xylene	4	8	3.4	50.0	8100
	6	4	3.6	54.4	7700

the quantity of glycol was added initially and the other half quantity added only after 2 hr. from the start of the reaction (Table IV). The fall in acid values with respect to time in the first set of experiments are shown in Figure 1.

In order to compare the performance of C.N.S.L. cation exchange resin as a catalyst in polyesterification with the performances as catalysts, of standard commercially available cation exchange resins, similar polyesterification experiments were carried out, with 2% of the resins in xylene. The results thus obtained are reported in Table V.

DISCUSSION

It is seen from Tables III and IV, that the results from the two sets of experiments are nearly identical. When the percentage of catalyst, in

TABLE V
Physical Properties of Polyesters Prepared in Xylene with
2% of Various Cation Exchange Resins as Catalyst (Time = 14 hr.)

Catalyst	Capacity, meq./g.	Acid number	Hydroxyl number	Viscosity cpoise	Color
Amberlite IR 120	4.0	32	100	7300	Brown
Amberlite IRC 50	10.0	95	120	950	Pale yellow
Zeo-Karb 215	2.0	12.45	63.8	5900	Pale yellow
C.N. S.L.	2.4	3.6	56.9	8000	Pale brown

benzene experiments was increased from 4 to 10%, the corresponding fall in acid value was from about 24 to about 10, i.e., nearly by half in 14 hr. When the percentage of catalyst was increased, in xylene experiments, from 4 to 6%, the time required to reach about 3.5 acid value fell down to nearly half, i.e., from 8 hr. to 4 hr.

Thus it is observed that with C.N.S.L. cation exchange resin a polyester with the desired properties can be prepared in about 4 hr. in xylene at normal pressure. It is also seen from Table V, that the efficiencies in decreasing order, of these cation exchange resins are, C.N.S.L. resin > Zeo-Karb 215 > Amberlite IR 20 > Amberlite IRC 50. C.N.S.L. resin and Zeo-Karb 215 belong to class of sulfonated phenol-formaldehyde type resin. Amberlite IRS 120 is a sulfonated polystyrene type resin and Amberlite IRC 50 is a free carboxylic type resin.

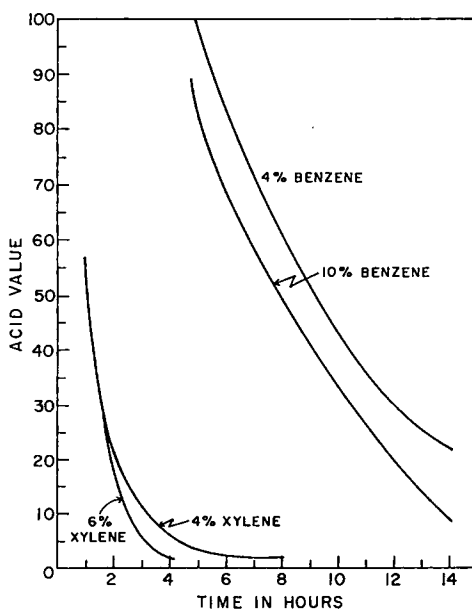


Figure 1.

Amberlite IRC 50, being a free carboxylic acid resin, is not an effective catalyst in polyesterification. Sulfonated polystyrene resins⁵ are reported to give preferentially higher yields of monesters of glycols under conditions where mineral acids give the diesters. It is therefore possible that Amberlite IR 120 may preferentially favor monoester formation in these experiments, resulting in a reaction product of high acid value. Sussman⁴ has reported higher yields of diesters and triesters by the use of the sulfonated coal type of cation exchange resin. It is therefore possible to assume that the sulfonated phenol-formaldehyde type resins favor the formation of polyesters, as shown by the polyesterification results of C.N.S.L. resin and Amberlite IR 120 in Table V. The lower acid value of the C.N.S.L. resin polyester may be due to the higher capacity of the C.N.S.L. resin compared to the Zeo-Karb 215 resin. These results thus suggest that the nature and the acid groups of the cation exchange resins do affect the course of reaction in the polyesterification.

CONCLUSIONS

Sulfuric acid, hydrochloric acid etc. are very cheap in comparison to cation exchange resins for use as catalysts in polyesterification. However, polyesters used for polyurethanes for end use in flexible foam products must be free from traces of acid catalysts. The use of cation exchange resins for polyesterification simplifies this problem. Being solid in nature, these resins are easily separated from the polyester by decantation or filtration. In spite of initial high cost of these resins they may compete with the cheap acid catalyst, because of their ability to be used again after regeneration. Since the polyesterification has been achieved at lower temperature, in a shorter time and at normal pressure, this method may develop into an economical method for polyester preparation.

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Résumé

Dans le but de préparer de la mousse de polyuréthane flexible, on a synthétisé des polyesters au moyen de la résine C.N.S.L. échangeuse de cations comme catalyseur dans le xylène. Avec 6% de résine C.N.S.L. le temps nécessaire pour atteindre le plus faible degré d'acidité, environ 3.5, est de 4 heures. En guise de comparaison on a employé 2% de résines échangeuses de cations—la résine C.N.S.L., Zéo-karb 215, Amberbite IR 20, Amberbite IRC 50, dans le xylène en vue de préparer les polyesters. Les résultats indiquent que dans ces polyesterifications la résine C.N.S.L. donne le plus faible degré d'acidité en 14 heures.

Zusammenfassung

Polyester zur Herstellung flexibler Polyurethan-Schaumstoffe wurden unter Verwendung des C.N.S.L.-Kationenaustauschharzes als Katalysator in Xylol als Reaktionsmedium hergestellt. Bei Verwendung von 6% des C.N.S.L.-Harzes beträgt die Zeit bis zur Erreichung der niedrigsten Säurezahl (etwa 3,5) vier Stunden. Zum Vergleich wurden 2% verschiedener Kationenaustauschharze, nämlich C.N.S.L.-Harz, Zeo-karb 215, Amberlite IR 20 und Amberlite IRC 50 in Xylol zur Herstellung der Polyester verwendet. Wie aus den Ergebnissen dieser Polyveresterungsversuche hervorgeht, wird mit C.N.S.L.-Harz die niedrigste Säurezahl nach 14 Stunden erreicht.

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