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Network Formation Involving Epoxide and Carboxyl Groups

Course of the Model Reaction Monoepoxide-Monocarbonic Acid

Libor Matějka, Svatopluk Pokorný and Karel Dušek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

Summary

The base catalyzed reaction between epoxide and carboxyl groups was studied using a simple model system phenylglycidyl ether-caproic acid in the presence of triethylamine. The reaction was investigated by mass spectrometry and GPC which provide an overall qualitative and quantitative survey of all the forming reaction products. The addition esterification is followed by etherification and condensation esterification and the main reaction product, monoester, is disproportionated yielding diester and diol. In a polyfunctional system, the latter reaction may cause splitting of the polymer chain and formation of new crosslinks.

Introduction

The reaction between the epoxide and carboxyl groups is one of the important reactions used in curing of epoxy resins. It is also used in the preparation of unsaturated polyesters of the acrylate or methacrylate type. In particular, however, this reaction is employed in the preparation of crosslinked elastomers from liquid carboxyl-terminated telechelic polymers and polyepoxides (HOFFMAN and GOBRAN 1973). The network properties are determined by the composition of the system, properties of the initial components, and mainly by the network structure which is dependent on the reaction mechanism. This is why it is necessary to know the course of the reaction as a function of the functionality and reactivity of the initial compounds and of their molar ratio, type and amount of the catalyst, temperature etc. Due to the complicated composition of products in polyfunctional systems, the mechanism of the crosslinking reaction can preferably be explained through a study of a model system represented by monoepoxide and monocarbonic acid.

The mechanism of the reaction between epoxide and carboxyl is rather complicated and has not yet been fully elucidated (MAY and TANAKA 1973). Generally, the reaction proceeds through the addition of the carboxyl

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to the epoxy groups with formation of monoester. This addition esterification is usually accompanied by side reactions. SHECHTER and WYNSTRA (1956) consider the following four reactions:

1) epoxide + acid → monoester (addition esterification)

2) epoxide + monoester → ether (etherification)

3) acid + monoester → diester + water (condensation esterification)

4) epoxide + water → glycol (hydrolysis)

In the reaction of carboxyl terminated telechelic polymers with polyfunctional epoxides, the addition esterification leads to chain extension, while etherification and condensation esterification cause branching and crosslinking. The relative rate of the first two reactions decides about the network density, and thus also about the mechanical properties of the product (condensation esterification is negligibly slow with respect to these reactions).

With an aim to verify the reaction scheme given above under the conditions of base catalysis, and especially in order to determine the relative significance of reactions leading to chain extension, formation of crosslinks or chain splitting, we investigated the base-catalyzed (triethylamine) reaction between epoxide and carboxyl using a simple model system phenylglycidyl ether-caproic acid.

Experimental

Chemicals. Caproic acid (CA) and phenylglycidyl ether (PGE) were distilled at reduced pressure and their purity was determined by gas chromatography - 99.7% (CA) and 99.6% (PGE). Triethylamine (TEA) was boiled with acetanhydride and redistilled (b.p. 360 K). Chromium (III) complex of diisopropylsalicylic acid (M_n = 2800 - VPO, 10wt.% Cr) was supplied by courtesy of Dr.Klásek, Institute of Chemical Technology, Gottwaldov.

1-Phenyloxypropanediol-3-caproate (monoester-M) was separated using a gel chromatograph from the reaction mixture prepared by heating of equimolar amounts of PGE with CA and 3.7wt.% TEA at 373 K for one hour.

1-Phenyloxypropanediol-2,3-dicaproate (diester-D) was obtained similarly by GPC separation from the reaction mixture PGE:CA=1:2 heated at 383 K for 8 h.

1-Phenyloxypropanediol (glycol-G) was prepared by hydrolysis of PGE in acetic acid in the presence of TEA and sulphuric acid. The reaction mixture (10 ml PGE, 30 ml CH_3COOH, 20 ml H_2O, 2 ml TEA and 0.5 ml H_2SO_4) was heated at 383 K for 8 h. The product was recrystallized from a mixture CH_2Cl_2 - hexane (m.p. 329 K). The composition and purity of the monoester, diester and glycol were checked by GPC analysis and mass spectrometry.

Analysis. The reaction mixtures were analyzed using GPC and the products were identified by mass spectroscopy.

GPC analysis was carried out on a gel chromatograph with five columns, 8x1200 mm in size, packed with the styrene-divinylbenzene copolymer S-Gel 832 (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences). Tetrahydrofuran was used as the elution agent; the qualitative and quantitative calibration was performed with pure standards. With oligomeric ethers, only qualitative results were obtained by this method, because the respective elution peaks are not sufficiently separated. An example of separation of the reaction mixture is given in Fig.1.

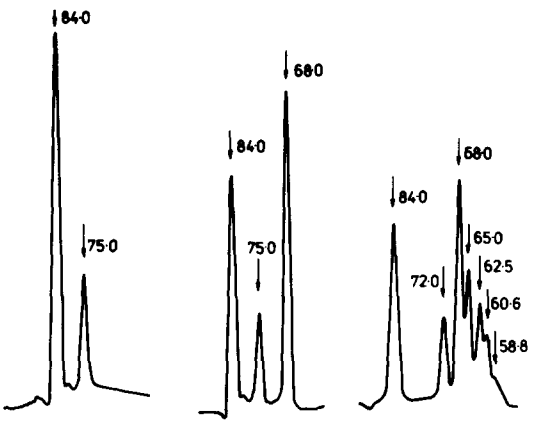
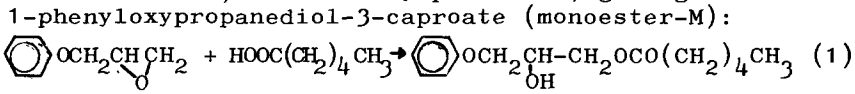


Fig.1. GPC record of the reaction mixture phenylglycidyl ether-caproic acid (T=358 K)
elution volumes (counts): phenylglycidyl ether 84.0, caproic acid 75.0, glycol 72.0, monoester 68.0, diester 65.0, ethers 62.5; 60.6 and 58.8

Mass spectra of the reaction products were obtained using an MS-902 mass spectrometer at the ion source temperature 413 K, electron emission 500 μA and energy 70eV. The method was used in particular in the determination of monoester and diester which are characterized by molecular ions with the respective mass numbers m/e 266 and 364 and by the intensive lines of fragments after the splitting-off of the phenyloxy group at m/e = 173 and 271.

Results and Discussion

When studying the reaction between phenylglycidyl ether (PGE) and caproic acid (CA), base catalyzed by triethylamine (TEA), we found that - as expected - the addition of the carboxyl to the epoxy group (addition esterification) is markedly preferred, giving rise to 1-phenyloxypropanediol-3-caproate (monoester-M):



(1)

In the initial stage, independently of the PGE to CA molar ratio, the addition esterification is the only reaction occuring in the system. Both reaction components are consumed at the same rate, and the monoester is the only reaction product (cf.Fig.2a-c).

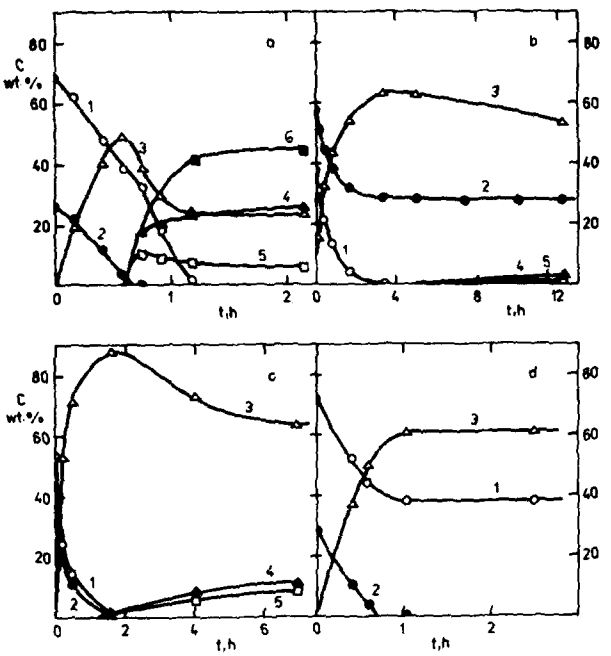
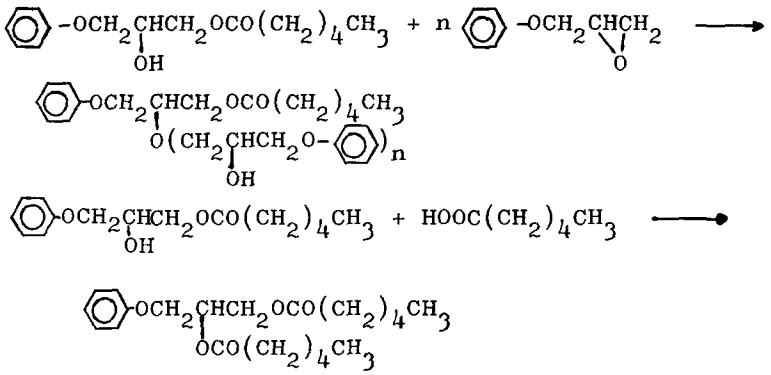


Fig.2 The change in the concentration of reaction components in the reaction between phenylglycidyl ether and caproic acid
1 PGE, 2 CA, 3 M, 4 D, 5 G, 6 ethers
2a: molar ratio PGE:CA=2.1, catalysis TEA (4.6 wt.-%), T=358K
2b: molar ratio PGE:CA=1:2, TEA (4.9 wt.-%), T=358K
2c: molar ratio PGE:CA=1:1, TEA (3.7 wt.-%), T=373K
2d: molar ratio PGE:CA=2:1, catalysis chromium (III) complex of diisopropylsalicylic acid (1wt.%), T=358 K

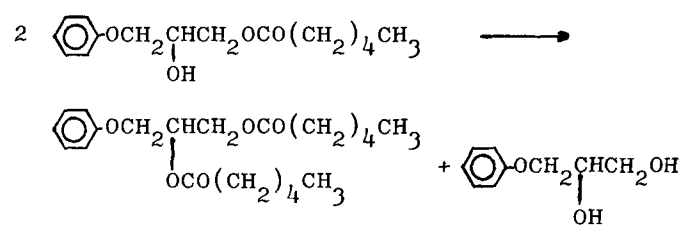
In the further stage, the reaction course depends on the molar ratio of the initial components. With PGE in excess, oligomeric ethers are formed in the reaction mixture after the acid has been consumed - reaction (2) (Fig.2a). With CA in excess after PGE has disappeared, the acid reacts with the monoester with formation of 1-phenyloxypropanediol-2,3-dicaproate (diester-D) - condensation esterification-reaction (3), (Fig.2b). Diester is also formed by reaction (4) described below:



(2)

(3)

The monoester content (Figs 2a,b) reaches a maximum during the reaction and then decreases as a result of the consecutive reaction mentioned above-etherification or condensation esterification. Fig.2c shows, however, that also in an equimolar mixture the monoester concentration passes through a maximum during the reaction. We found that in this case the loss of monoester was due to its disproportionation to diester and 1-phenyloxypropanediol (glycol-G) (4)



(4)

Both these compounds were identified in the reaction mixture by means of GPC and mass spectrometry. The mass spectra of the respective fractions isolated by GPC contain molecular ions, and their total fragmentation corresponds to the monoester and glycol.

Figs 2a-c show that in the base-catalyzed reaction between PGE and CA, both etherification and disproportionation become operative only after the acid has reacted, even with PGE present in excess. The effect of the catalyst type-TEA and the chromium(III) complex of diisopropylsalicylic acid - on the course can be seen from Figs 2a,2d. The chromium(III) catalyst is obviously very selective for the addition esterification, because etherification or disproportionation has not been observed even after all the acid had been consumed.

Using these results, the reaction scheme given

above must be supplemented by the disproportionation reaction:

monoester ⟶ diester + glycol

Therefore, the reaction of PGE and CA with glycol leading to the formation of ethers, or of monoester and water should also be considered.

Conclusion

An investigation of the model reaction has demonstrated that only addition esterification proceeds in the initial stage in a base-catalyzed system. Further reactions - etherification, condensation esterification, and disproportionation are consecutive and become operative only after the acid or epoxide has been consumed; of these, etherification is the fastest. While etherification and condensation esterification require the presence of unreacted epoxide or carboxyl groups, disproportionation proceeds also after these groups have been consumed. In a polyfunctional system, this reaction may significantly affect the network structure (heterogeneity) by simultaneously breaking the chains and giving rise to new crosslinks.

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