Benzil–benzilic acid rearrangement in crosslinked macromolecular systems: effect of crosslinking

Sunny Kuriakose and V. N. Rajasekharan Pillai*
School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, Kerala, India
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The effect of the molecular character and extent of crosslinking units on polymer-analogous benzil–benzilic acid rearrangement was investigated. A typical hydrophobic styrene–divinylbenzene copolymer and a hydrophilic styrene–tetraethyleneglycol diacrylate copolymer were used as the polymer supports. Supports with crosslink densities varying from 2 to 20% were functionalized. The polymer-bound aldehydes were subjected to crossed benzoin condensation in the presence of benzaldehyde. The benzoin analogues were converted to benzils and then subjected to benzil–benzilic acid rearrangement. The products were characterized by i.r. and ^{13}C n.m.r. spectroscopy and the extent of rearrangement was determined by chemical methods.

(Keywords: benzilic acid; crosslinking; rearrangement)

Introduction

The macromolecular structural features of polymeric support materials have been shown to contribute significantly to the reactivity of the functional groups. The specificity of the functional polymeric species is achieved by the unique interaction of the macromolecular support with the functional groups. The polymer support must possess a structure that permits enough diffusion of the substrates into the interior reactive sites. This is related to the swelling pattern of the matrix, effective pore size and pore volume, and rigid or flexible nature of the polymer[1–4]. By a proper choice of the monomer, crosslinking agent and reaction conditions, it is possible to construct a polymer matrix with the desired molecular structure, stereochemistry, flexibility, solvation and mechanical stability[5]. The extraneous conditions necessary in a solution-phase method for effecting specific reaction can be built into the macromolecular matrix by keeping the advantages of the polymer as a support material[6–8]. In polymer-analogous benzil–benzilic acid rearrangement, the migration process is initiated by the attack of hydroxide ion on the carbonyl carbon of the diketo group. The rate and extent of the rearrangement are related to the accessibility of the anionic attacking species to the migration origin, and this in turn is related to the molecular character and rigidity of the polymeric matrix. These factors are subjected to investigation here using a series of polymeric α-diketones.

Results and discussion

The styrene–divinylbenzene (DVB) and styrene–tetraethyleneglycol diacrylate (TTEGDA) copolymers were subjected to functional transformations for introducing a rearrangeable α-diketo group into the polymer matrix. The polymers were chloromethylated by using $SnCl_4$ and chloromethyl methyl ether. These chloromethyl resins were converted to polymeric aldehydes by treating with dimethylsulfoxide in the presence of sodium bicarbonate. The resulting aldehyde analogues[9] were subjected to crossed benzoin condensation with benzaldehydes in the presence of potassium cyanide (*Scheme 1*).

A diketo group was introduced into the polymer matrix by oxidizing the α-hydroxy ketone by treating with copper(II) acetate, ammonium nitrate and aqueous acetic acid. The benzil analogues were obtained in almost quantitative yield (*Scheme 1*). The i.r. spectrum shows a strong band at 1690 cm^{-1} corresponding to the C=O stretching vibration. The spectrum appears as a single peak in this region with a shoulder. This observation suggests a *trans* configuration for the dicarbonyl groups[10]. Therefore both the carbonyl groups are not i.r. active. This configuration is attributable to the rigidity of the polymer backbone and the resulting spatial strain. The ^{13}C cross polarization/magic angle spinning (CP/MAS) n.m.r. spectrum shows a peak at 173.6 ppm and this was assigned to the carbon atoms of the dicarbonyl group. The ring carbons exhibit a characteristic peak at 126 ppm. The benzil analogues were subjected to the benzil–benzilic acid rearrangement under basic conditions (*Scheme 1*).

Effect of the nature of crosslinking. The molecular characteristics of the crosslinking agents, such as its polarity, hydrophilicity and rigidity, were found to affect the migratory aptitude of the rearrangeable functions. For a comparative study, two different types of polymer supports were employed. Polystyrene (PS)–DVB resin is a typical hydrophobic polymer with rigid crosslinking units. On the other hand, PS–TTEGDA resin is a hydrophilic and polar polymer support with flexible crosslinking. The diketo groups attached to both polymers were subjected to rearrangement under identical reaction conditions. Dioxane was used as the solvent for PS–TTEGDA resin whereas toluene was used as the solvent for PS–DVB resin. The results are presented in *Table 1*.

The results can be explained on the basis of the crosslinking pattern of the two polymer networks. The reactive sites are buried deep in the rigid polymer network in the case of PS–DVB resin and the diffusion-controlled movement of the hydroxide ion into the interior of the

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*To whom correspondence should be addressed

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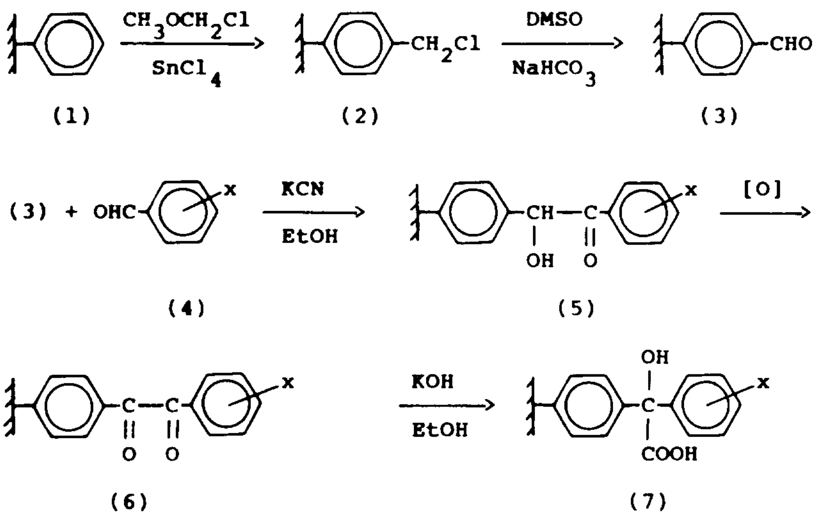

Scheme 1 Synthesis of polymeric α-diketone and its rearrangement to benzilic acid

Table 1 Effect of the nature of crosslinking on benzil–benzilic acid rearrangement

Crosslink density (%)	Crosslinking agent	Duration of reaction (h)	Solvent	Percentage migration (%)
5	DVB	75	Toluene	82.3
5	TTEGDA	60	Dioxane	85.2
10	DVB	75	Toluene	74.0
10	TTEGDA	60	Dioxane	75.0
15	DVB	75	Toluene	54.5
15	TTEGDA	60	Dioxane	60.0

Table 2 Effect of the DVB content on the extent of rearrangement

Crosslink density (%)	Diketo capacity of benzil (meq g^{-1})	Hydroxyl capacity of benzilic acid (meq g^{-1})	Percentage migration (%)
2	1.80	1.7	94.4
5	1.70	1.4	82.3
10	1.35	1.0	74.0
15	1.10	0.6	54.5
20	0.80	0.2	25.0

polymer is difficult. But the reactive sites are more available to the reagent in the case of PS–TTEGDA resin owing to its less rigid nature.

Effect of the degree of crosslinking. The microenvironmental effect of the polymeric backbone on the extent of migration of the rearrangeable functional group attached to it is determined by the frequency of crosslinking units within the matrix. A correlation between the percentage migration and extent of crosslinking was obtained from two different polymer supports with varying crosslink densities.

PS–DVB resins with crosslink densities of 2, 5, 10, 15 and 20% were prepared, and were converted to the corresponding benzil analogues by a series of polymer analogous reactions. Benzaldehyde was used for preparing mixed benzoins. Rearrangement was carried out under identical conditions using toluene as the solvent. The product was characterized by i.r. and ^{13}C n.m.r. spectroscopy.

In the i.r. spectrum, the carbonyl absorption remains strong and intense in the region 1680–1700 cm^{-1} with a small shift to the higher wavenumber region. A broad peak appeared in the region 3380–3440 cm^{-1} corresponding to the O–H stretching absorption. The peaks at 1270 and 1090 cm^{-1} correspond to the O–H deformation and C–O stretching vibrations, respectively. The carbon atom bonded to the hydroxyl and carboxyl groups shows a characteristic peak at 89.2 ppm in the ^{13}C n.m.r. spectrum[11,12]. The peak at 173.6 ppm in the benzil analogue was shifted to 166 ppm. The low-field shift of the carbonyl carbon clearly indicates the generation of the carboxyl group. The percentage migrations were calculated by chemical methods (*Table 2*).

Table 3 Effect of TTEGDA content on benzil–benzilic acid rearrangement

Crosslink density (%)	Diketo capacity of benzil (meq g^{-1})	Hydroxyl capacity of benzilic acid (meq g^{-1})	Percentage migration (%)
5	1.7	1.45	85.2
10	1.6	1.20	75.0
15	1.5	0.90	60.0
20	1.3	0.50	38.4

Diketo function was introduced into the hydrophilic PS–TTEGDA resins with crosslink densities of 5, 10, 15 and 20%. Polar solvents are more compatible with the polar polymer matrix and the reaction is carried out in dioxane under identical conditions. The hydroxy acid formed by the rearrangement was estimated. The results are given in *Table 3*.

Diketo systems attached to PS–DVB and PS–TTEGDA resins show a regular decrease in the extent of rearrangement with increase in crosslink density. The results can be explained as arising from the increased rigidity of the polymer matrix and hence the poor accessibility of the reagent to the reactive sites, rather than from the steric participation of the polymeric matrix on the course of the rearrangement. The diffusion-controlled penetration of the reagent into the interior of the matrix is prevented by the high-frequency crosslinks. The decrease in the extent of rearrangement with increased degree of crosslinking is more prominent in the case of PS–DVB resin owing to the high rigidity of the matrix. Hydrolysis of ester crosslinking units was observed to some extent in the case of PS–TTEGDA resin. Owing to this hydrolytic reaction, unexpectedly high functional group capacities were recorded in the estimation processes. Hence, a control experiment was conducted in the case of PS–TTEGDA resin and this functional group value was subtracted from the final values (*Table 3*).

Experimental

Styrene, DVB and TTEGDA were commercially available samples (Merck, Germany). Styrene–DVB copolymers were prepared by suspension polymerization and styrene–TTEGDA copolymers by solution polymerization. Polymeric aldehyde was synthesized by the literature procedure[9]. Hydroxyl group was estimated by acetylation method. I.r. spectra were recorded on a Shimadzu-470 spectrophotometer and ^{13}C CP/MAS solid state n.m.r. measurements were conducted on a Bruker 300 MSL CP/MAS instrument operating at 75.47 MHz.

Preparation of polymeric benzoin. A mixture of polymeric aldehyde (5 g), benzaldehyde (three-fold molar excess), dimethylformamide (DMF) (25 ml), absolute ethanol (20 ml) and potassium cyanide (0.75 g) in 10 ml water was heated at 110°C for 60 h with stirring. The mixture was cooled, filtered and washed with water, water–dioxane, dioxane and finally with dichloromethane. Drying under vacuum afforded polymeric benzoin.

Preparation of polymeric benzil. A mixture of polymeric benzoin (5 g), copper (II) acetate (0.2 g), ammonium nitrate (2.5 g) and 80% aqueous acetic acid (50 ml) was heated at 100°C for 40 h with stirring. The reaction mixture was cooled, filtered and washed with water, water–dioxane, ethanol and finally with acetone. Drying under vacuum afforded 4.95 g polymeric benzil.

Preparation of polymeric benzilic acid by benzil–benzilic acid rearrangement. A mixture of polymeric benzil (5 g), KOH (0.8 g) in 20 ml water, DMF (40 ml) and absolute ethanol (30 ml) was heated at 105°C for 75 h with stirring. The reaction mixture was cooled, filtered and washed with water. The resin was stirred with 4N HCl–dioxane mixture (1:1, 50 ml) for 6 h. This was filtered, washed with water, dioxane–water, dioxane and finally with dichloromethane. Drying under vacuum afforded 4.9 g of polymeric benzilic acid.

Conclusion

These investigations indicate that a rearrangeable functional group attached to a crosslinked polymeric support can undergo intramolecular migrations under suitable conditions. The molecular properties and morphological characteristics of the backbone are decisive factors in controlling the migratory aptitudes. However, the rearrangement can be affected in these macromolecular networks as in any other polymer-supported reactions. In polymer-analogous molecular rearrangements, the polymer provides a unique microenvironment for the rearrangeable functional groups and thus participates in the course of the rearrangement. The attack of the anionic species on the migration origins is a diffusion-controlled reaction. Since the characteristic diffusion process depends on the nature of the polymer sample, the crosslink density and molecular character of the crosslinking units become decisive factors. The accessibility of the hydroxide ion, and therefore the percentage migration, thus depend on the crosslinking units and monomer/crosslinker ratio.

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