Effects of Cyclodextrins on the Radiation-induced Polymerization of Sodium p-Styrenesulphonate in Aqueous Solution

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Radiation-induced polymerization of sodium p-styrenesulphonate in aqueous solution is accelerated by γ-cyclodextrin and is inhibited by α-cyclodextrin through binding of the propagating radical chain ends into the cyclodextrin cavities.

Cyclodextrins (CDs) possess hydrophobic cavities and form inclusion complexes with various organic molecules in aqueous solution.[1,2] Inclusion complexes involving two guest molecules in a single cavity are well characterized for γ-CD, which has a large cavity compared with α- and β-CDs. The complexation of aromatic substrates by γ-CD promotes the formation of excimers.[3—7] It has also been reported that Diels–Alder reactions are accelerated by β-CD through hydrophobic binding of the reactants into the cavity, but not by α-CD, which has a smaller cavity.[8,9] This communication reports the effects of the CD complexation of propagating radicals on the polymerization of sodium p-styrenesulphonate (p-SS) in aqueous solution. The polymerization was initiated by γ-irradiation without using conventional radical initiators in order to eliminate any additional effect due to the complexation of the initiators by CDs.

The radiation-induced polymerization was carried out using a ^{60}Co source (dose rate, 5×10^2 Gy h^{-1}). The effects of α- and γ-CDs added to an aqueous solution of p-SS (4.8 wt%) were examined under an atmosphere of nitrogen at room temperature. β-CD was not used because of its lower solubility in water. Pulse radiolysis experiments were undertaken to investigate the effects of the CDs on the lifetime of the propagating radicals under the same conditions as the polymerization experiments. An L-band linear accelerator operating at 28 MeV and at a pulse width of 8 ns was used for the pulse radiolysis.

Figure 1 shows the time–conversion curves for the polymerization in the absence and presence of the CDs. The conversions were determined by measuring the 255 nm absorption due to the monomer. The decrease in this absorption, caused by the irradiation, was accompanied by an increase in the 225 nm absorption due to the polymer. The polymerization is accelerated by γ-CD and is retarded by α-CD. The G values for monomer consumption at an irradiation time of 15 min were 2.4×10^2 and 1.2×10^5 for the CD-free and γ-CD-added solutions, respectively; the G value represents the number of the consumed monomer molecules per 100 eV energy absorbed by the medium. Figure 2 shows the dependence of the conversion on the CD concentration. For the γ-CD system, appreciable acceleration is attained up to [CD]/[p-SS] of 1/2 (mol/mol). This might be attributed to the contribution of a 1:2 γ-CD-p-SS complex.

It is known that the propagating radicals of styrene derivatives have an absorption band at around 320 nm.[10] Figure 3 shows the decay curves of the 320 nm absorption observed by pulse radiolysis of the CD-free and CD-added solutions. The decay of the propagating radicals becomes slow in the presence of the CDs. This indicates that the propagating chain ends are included in the CD cavities. The retarding effect is more significant with γ-CD than with α-CD. The yield of the propagating radicals is slightly decreased by the addition of the CDs. The initiating species produced in the irradiated aqueous solutions are H atoms and OH radicals; G values 0.6 and 2.95, respectively.[11] It is natural to consider that a fraction of the initiating species reacts with the CDs to give the less

reactive CD radicals, α-hydroxyalkyl-type radicals, through hydrogen abstraction. The binding of the hydrophobic vinyl groups of the monomer molecules is also considered to be responsible for the decrease in the propagating radical yield.
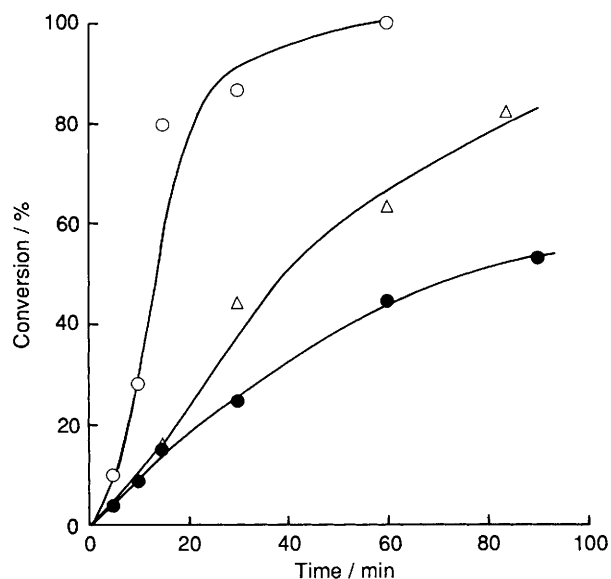

Figure 1. Time–conversion curves for the aqueous solutions of p-SS in the absence (△) and presence of α-CD (●) and γ-CD (○): [CD]/[p-SS], 1/2 (mol/mol).
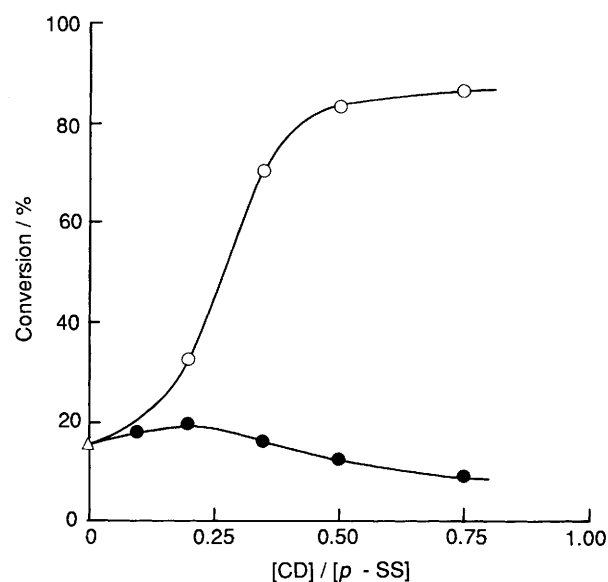

Figure 2. Dependence of the conversions on the concentration of α-CD (●) and γ-CD (○) at an irradiation time of 15 min.

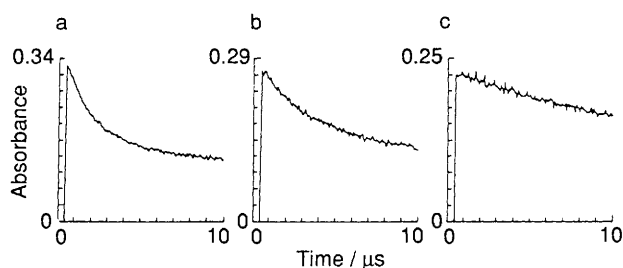**Figure 3.** Decay behaviour of the 320 nm absorption due to the propagating radicals in the absence (a) and presence of α-CD (b) and γ-CD (c): [CD]/[p-SS], 1/2 (mol/mol).

The results obtained in this study can be interpreted in terms of the binding of the propagating chain ends within the CD cavities as follows. For the α-CD complex, the propagation reaction is inhibited as well as the bimolecular termination reactions because of the small size of the CD cavity. On the other hand, in the larger γ-CD cavity, the propagation reaction is not inhibited because of the binding of both the propagating chain end and the vinyl group of the monomer molecule. The hydrophobic effect accelerates the propagation reaction as reported for the Diels–Alder reactions.[8,9] The bimolecular termination reaction is inhibited by the binding of the propagating chain ends in the CD cavities. The inhibition of the termination reaction enhances the polymerization in the γ-CD system as well as the hydrophobic effect.

The decay of the propagating radical was more markedly retarded by γ-CD than by α-CD (Figure 3). At a [CD]/[p-SS] ratio of 1/2, both the complexed and dissociated radicals are

formed and contribute to the recombination reaction in the α-CD system. However, if the formation of the 1:2 γ-CD-p-SS complex is favoured, the termination reaction occurs between the complexed radicals in the γ-CD system. This might explain the difference between the α- and γ-CD systems.

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