Hydrophobic Acceleration of *p*-Styrenesulfonate Polymerization by γ-Cyclodextrin

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Radiation-induced radical polymerization of *p*-styrenesulfonate (SS) in aqueous solution is accelerated in the presence of γ-cyclodextrin (γ-CD). The polymer yield tends to be independent of γ-CD concentration above [γ-CD]/[SS] = 0.5, indicating that γ-CD forms a 1:2 complex with SS to promote the polymerization. *p*-Ethylbenzenesulfonate (EBS) suppresses the accelerating effect of γ-CD. This is attributed to competitive complexation of EBS with γ-CD. Molecular weight of the polymer becomes higher in the presence of γ-CD. Molecular weight distribution curves of the polymers obtained at [γ-CD]/[SS] = 0.15–0.30 are clearly bimodal, suggesting contributions of complexed and dissociated propagating radicals. An aggregation of the 1:2 complexes is proposed to account for the independent propagation of the complexed and dissociated radicals. Glucose (Glc), a component unit of CDs, also accelerates the polymerization, but to a smaller extent than γ-CD. The polymer yield continues to increase with Glc concentration up to [Glc]/[SS] = 6, and is hardly affected by EBS. A hydrophobic aggregation of SS may be responsible for the acceleration of the polymerization in the presence of Glc.

Cyclodextrins (CDs) are cylindrical compounds composed of glucose (Glc) units and form inclusion complexes with various organic molecules in aqueous solution.[1,2] The most common of them are α-, β- and γ-CDs consisting of six, seven and eight Glc units, respectively. The host–guest stoichiometry depends on sizes of CD cavities and of guest molecules. The hydrophobic association involving two guest molecules in a single cavity accelerates bimolecular reactions such as Diels–Alder reactions[3-5] and photodimerization.[6] On the other hand, 1:1 complexation of reactants with CDs having smaller cavities inhibits bimolecular reactions.

In the preceding communication we have reported the effects of the CD complexation on the radiation-induced polymerization of *p*-styrenesulfonate (SS) in aqueous solution.[7] The polymerization is accelerated in the presence of γ-CD and is decelerated in the presence of α-CD; the effect of β-CD was not examined because of the low solubility. A pulse radiolysis study has suggested that the propagating radicals are produced in the CD cavities to be protected against bimolecular termination. A 1:2 complex is considered to be formed between γ-CD and SS to promote the polymerization. On the other hand, the propagation of the radicals is inhibited by the complexation with α-CD.

In the present study the effect of γ-CD is investigated in detail and is compared with that of Glc. Molecular weight distributions of the polymers were measured to reveal the effect of the CD complexation on the propagating step.

Experimental

Sodium salt of SS and α-CD (both Wako Chemicals) were recrystallized from water–methanol mixtures. Sodium salts of *p*-ethylbenzenesulfonate (EBS) and benzenesulfonate, γ-CD and glucose (Glc) (all Wako Chemicals) were used without further purification. Water was deionized and then distilled.

The polymerization was carried out at a monomer concentration of 0.25 mol dm^{-3}. The pH values of the solutions for the polymerization experiments were in the range 8.9–9.7. The solutions, saturated with nitrogen, were irradiated with ^{60}Co γ-rays at a dose rate of 5 × 10^{2} Gy h^{-1} and at 0 °C unless otherwise noted. Polymer yields were determined by measuring the 255 nm absorption due to the monomer. The decrease in the monomer absorption was accompanied by an increase in the 225 nm absorption due to the polymer. Gel permeation chromatography of the polymers was performed on TSK-Gel 6000 PW$_{XL}$ and 3000 PW$_{XL}$ columns connected in series with a mixed water–acetonitrile solution (9:1 in volume) of 0.1 mol dm^{-3} NaNO$_3$ as an eluent at a flow rate of 1.0 cm^3 min^{-1}. The molecular weights of the polymers were calculated by using a calibration curve based on sodium poly(*p*-styrenesulfonate) standards (Polymer Laboratories, M_n = 5400–780 000).

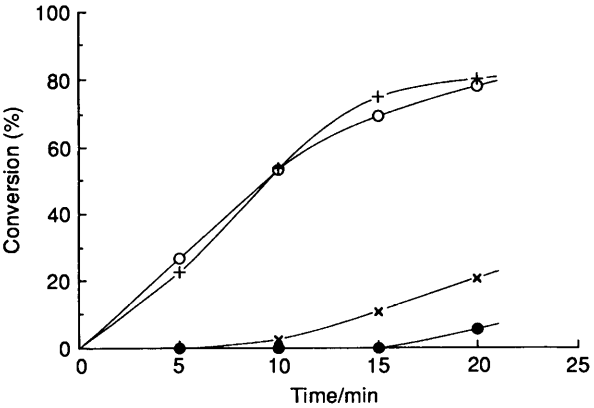

Fig. 1 Time–conversion curves for the aqueous solution of SS (0.25 mol dm^{-3}) at a dose rate of 5 × 10^{2} Gy h^{-1}. Additive and temperatures: (○) γ-CD (0.125 mol dm^{-3}), 0 °C; (+) γ-CD (0.125 mol dm^{-3}), 20 °C; (●) none, 0 °C; (×) none, 20 °C.

Results and Discussion

γ-Irradiation can initiate the radical polymerization at arbitrary temperature without using conventional radical initiators and is favourable for investigating the effect of the CD complexation of the monomer alone. The initiating species produced in the irradiated aqueous solutions are H atoms and OH radicals.[8] The radiation-induced polymerization is greatly accelerated in the presence of γ-CD. Fig. 1 shows the effect of γ-CD on the time–conversion curves at [γ-CD]/[SS] = 0.5 and at 0 and

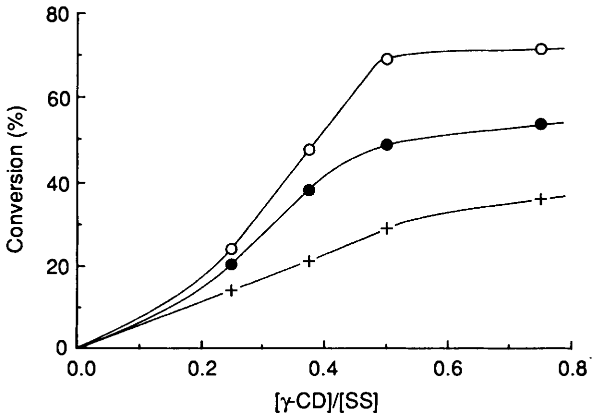

Fig. 2 Dependence of the polymer yield on γ-CD concentration at irradiation times of (+) 6 min, (●) 12 min, (○) 15 min at 0 °C: [SS] = 0.25 mol dm^{-3}

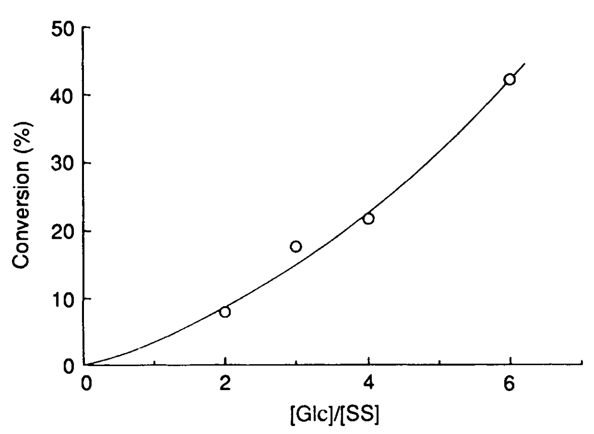

Fig. 3 Dependence of the polymer yield on Glc concentration at an irradiation time of 15 min at 0 °C: [SS] = 0.25 mol dm^{-3}

20 °C. The polymer yields for the solution containing γ-CD seem to be almost independent of temperature, whereas those for the CD-free solution are higher at 20 °C than at 0 °C. That is to say, the apparent activation energy of the radical polymerization is decreased in the presence of γ-CD. This may be attributed to an increase in the association constant of the inclusion complex at the lower temperature, as is generally observed for CD complexation. Promotion of the aggregation of the CD complexes, proposed below, at the low temperature may also be responsible for the temperature dependence.

Fig. 2 shows the dependence of the polymer yields on γ-CD concentration at different irradiation times, 6, 12 and 15 min. A trend is observed that the polymer yields become constant above [γ-CD]/[SS] = 0.5 irrespective of the irradiation times, suggesting the contribution of the 1 : 2 complex to the polymerization. The polymer yield decreased in the presence of α-CD; the yields in the absence and presence of 0.125 mol dm^{-3} α-CD were 41 and 28%, respectively, at an irradiation time of 60 min and at 0 °C.

The polymerization was also accelerated by Glc, but the effect was much smaller than that of γ-CD when compared at the same concentrations. Fig. 3 shows the dependence of the polymer yield on Glc concentration at an irradiation time of 15 min. In contrast with the case of γ-CD, no saturation is observed in the concentration dependence up to [Glc]/[SS] = 6 examined. An aggregation of the hydrophobic styryl groups in the presence of Glc may be responsible for the acceleration of the polymerization.

Fig. 4 shows the changes in polymer yield caused by the addition of sodium EBS to the solutions containing α- and γ-CDs and Glc. The polymer yield in the presence of γ-CD is decreased by EBS. This can be attributed to the complexation of EBA competing with that of SS. On the other hand, the polymer yield in the presence of α-CD is increased by EBS, demonstrating that the inhibition of the polymerization by α-CD is also due to the CD complexation. As expected, the polymer yield for the solution containing Glc is hardly affected by EBA, and nor is that for the pure SS solution. Similar results were obtained with sodium benzenesulfonate added to the solutions containing γ-CD and Glc; for the solution containing α-CD the effect of benzenesulfonate could not be examined because of the deposition of the inclusion complex. For the solution containing γ-CD the relative polymer yields at [EBS]/[SS] above 1.5 are about 0.5 and almost constant, although at the irradiation time of 15 min no polymer is obtained in the pure SS solution. This means that the acceleration of the polymerization in the presence of γ-CD is not only due to the 1 : 2 complexation but also due to some additional effect not disturbed by EBS. A hydrophobic aggregation similar to the case of Glc may be responsible for the accelerating effect of γ-CD. An aggregation of the 1 : 2 complexes is suggested by the molecular weight distributions of the polymers as described below.

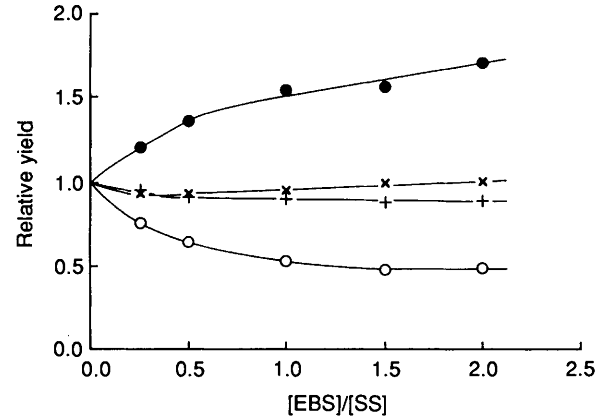

Fig. 4 Polymer yields relative to those in the absence of EBS plotted against [EBS]/[SS] for the SS (0.25 mol dm^{-3}) solutions at 0 °C. Additives and irradiation times: (○) γ-CD (0.125 mol dm^{-3}), 15 min; (●) α-CD (0.125 mol dm^{-3}), 60 min; (+) Glc (1.0 mol dm^{-3}), 30 min; (×) none, 60 min.

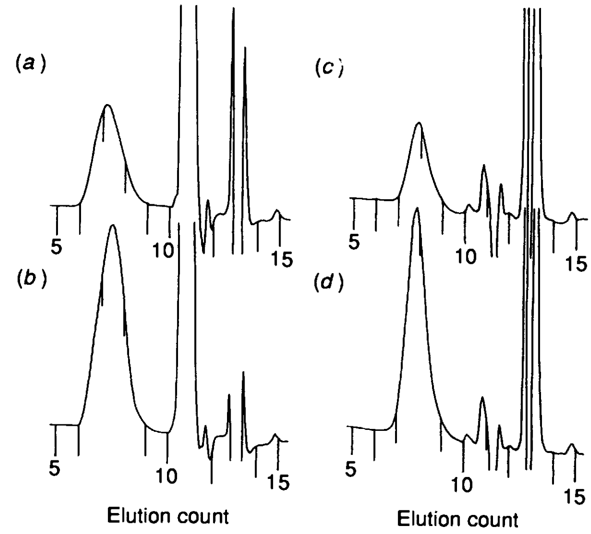

Fig. 5 Gel permeation chromatograms for the SS (0.25 mol dm^{-3}) solutions irradiated at 0 °C. Additive and irradiation times: (*a*) γ-CD (0.125 mol dm^{-3}), 6 min; (*b*) γ-CD (0.125 mol dm^{-3}), 15 min; (*c*) none, 30 min; (*d*) none, 60 min.

Fig. 5 shows the gel permeation chromatograms for the solutions irradiated in the absence and presence of γ-CD ([γ-

Table 1 Effects of CDs and Glc on the molecular weights of polymers obtained at 0 °C

Additive (mol dm^{-3})	Irradiation time/min	Conversion (%)	M_n	M_w/M_n
none	30	19	4.4×10^4	2.5
none	60	41	4.1×10^4	3.1
none	120	82	4.2×10^4	2.8
γ-CD (0.125)	6	31	1.3×10^5	4.0
γ-CD (0.125)	12	62	1.0×10^5	4.1
γ-CD (0.125)	30	87	5.3×10^4	3.8
α-CD (0.125)	60	28	2.6×10^4	2.6
α-CD (0.125)	120	49	2.4×10^4	2.4
Glc (1.0)	15	18	1.0×10^5	3.0
Glc (1.0)	30	45	1.1×10^5	2.9
Glc (1.0)	60	73	1.0×10^5	2.7

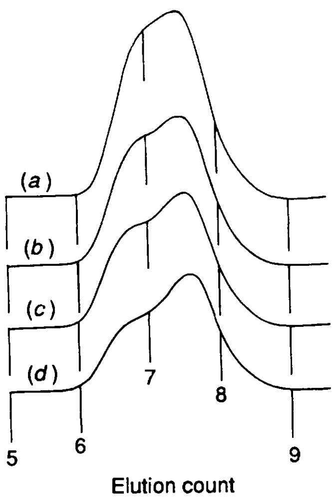

Fig. 6 Molecular weight distributions of the polymers produced in the SS (0.25 mol dm^{-3}) solutions containing γ-CD at an irradiation time of 15 min at 0 °C: [γ-CD]/[SS]; (*a*) 0.30, (*b*) 0.25, (*c*) 0.20, (*d*) 0.15

CD]/[SS] = 0.5); the solutions were submitted to chromatography after dilution with ten-fold volume of the eluent solution. The peaks at elution counts of 7–8 are assigned to the polymers and those at around 11 and 14, superposed with impurity peaks (ghost peaks), are assigned to γ-CD and the monomer, respectively. It can be seen that higher molecular weight polymers are produced in the presence of γ-CD. The values of M_n and M_w/M_n are listed in Table 1 together with those for the solutions containing α-CD and Glc. The M_n values of the polymers produced in the presence of γ-CD decrease with irradiation time, whereas those for the other systems are independent of irradiation time. The M_w/M_n ratios for the γ-CD system are also larger than those for the other systems. The M_n value increases in the presence of Glc, whereas it decreases in the presence of α-CD.

Fig. 6 shows the molecular weight distribution curves of the polymers obtained at [γ-CD]/[SS] = 0.15–0.30. They are clearly bimodal indicating a contribution of propagating species having different reactivities to the polymerization. The relative height of the higher molecular weight peak increases with increasing γ-CD concentration. Thus, the higher molecular weight peak is assigned to a product of the complexed propagating radicals, and the lower one to a product of the dissociated propagating radicals. The independent propagation of the complexed and dissociated radicals can be explained by assuming an aggregation of the 1:2 complexes of SS with γ-CD. That is to say, the 1:2 complexes and the dissociated SS polymerize separately through aggregation at these γ-CD concentrations.

The radiation chemical yields, *G* values, of the initiating species are 0.6 and 2.7 for H and OH, respectively.[8] The symbol *G* represents a number of molecules produced or consumed per 1.6021×10^{-17} J absorbed energy. The *G* values for polymers, *G*(polymer), were calculated from the *G* values for the monomer consumption and the M_n values. The *G*(polymer) values in the presence of γ-CD were in the range 24–33. The number of polymer molecules per initiating radical, *G*(polymer)/*G*(radical), is 7.3–10. This corresponds to the minimum yield since all of H and OH could not initiate the polymerization in the presence of γ-CD which reduces the yield of the propagating radicals as shown previously by the pulse radiolysis experiments.[7] The large *G*(polymer)/*G*(radical) values suggest that the chain transfer to the monomer occurs, and that the molecular weights of the polymers depend mainly on the competition between the propagation and the chain transfer to the monomer, but are hardly affected by the termination. This means that the formation of the higher molecular weight polymers is attributed to an acceleration of the propagation and/or a deceleration of the chain transfer to the monomer in the presence of γ-CD. The chain transfer to γ-CD may also occur but should not be important since the M_n value increases in the presence of γ-CD.

It is interesting that the propagating radical is included in the γ-CD cavity resulting in the change in reactivity. The propagation is the addition of the α-carbon of the propagating radical to the β-carbon of the monomer, whereas the chain transfer is the H-transfer from the β-carbon of the propagating radical to the β-carbon of the monomer. Therefore, higher molecular weight polymers are produced if the α-carbon of one of the monomers in the 1:2 complex is close to the β-carbon of another monomer and the β-carbons are separated from each other in the γ-CD cavity. Thus, a possible explanation of the formation of the higher molecular weight polymers is the configuration of the monomers in the γ-CD cavity of the 1:2 complex. The decrease in the M_n value with irradiation time, occurring only in the presence of γ-CD, may be due to the 1:1 complexation, which becomes important as the monomer concentration decreases during the polymerization.

For the solution containing α-CD the *G*(polymer)/*G*(radical) value is about 3.1. In this case the M_n value seems to depend on the competition between the propagation and the termination as well as on the competition between the propagation and the chain transfer. Thus, the suppression of the propagation by the complexation of the monomer with α-CD may result in the decrease in the M_n value. Similarly, in the presence of Glc, the *G*(polymer)/*G*(radical) value is less than 2.5, and the increase in the M_n value may be attributed to the promotion of the propagation by the hydrophobic aggregation.

Conclusions

The radiation-induced radical polymerization of SS is accelerated in the presence of γ-CD. The contribution of the inclusion complexes is demonstrated by the effect of EBS. The dependence of the polymer yield on γ-CD concentration suggests 1:2 host–guest complexation. The aggregation of the 1:2 complexes is proposed to account for the independent propagations of the complexed and dissociated radicals resulting in the bimodal molecular weight distributions of the polymers obtained at [γ-CD]/[SS] = 0.15–0.30. The accelerating effect of Glc is also interpreted in terms of the hydrophobic aggregation. The formation of the higher molecular weight polymers in the presence of γ-CD may be attributed to the configuration of SS in the 1:2 complexes.

References

1 M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, Berlin, 1978.
2 J. Szejtli, *Cyclodextrins and Their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982.
3 D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.*, 1980, **102**, 7817.
4 N. K. Sangwan and H.-J. Schneider, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1223, and references cited therein.
5 I. Hunt and C. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1051.
6 F. Hirayama, T. Utsuki and K. Uekama, *J. Chem. Soc., Chem. Commun.*, 1991, 887.
7 D. Gau, Y. Yamamoto and K. Hayashi, *J. Chem. Soc., Chem. Commun.*, 1990, 910.
8 G. V. Buxton, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, eds. J. H. Baxendale and F. Busi, D. Reidel, Dordrecht, 1982, p. 241.

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