

Chain transfer and molecular weight in the ionizing radiation initiated cationic polymerization of styrene derivatives

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Summary

A strong effect of monomer structure on molecular weight is found in the radiation initiated cationic polymerization of para substituted styrene derivatives. This effect is proposed to result from steric hindrance in the chain transfer reaction. The conclusion is reached that the predominant chain transfer reaction under the conditions employed is attack by the cation on the monomer aromatic ring rather than by intramolecular attack on the penultimate aromatic ring of the propagating chain.

Introduction

Molecular weight in cationic polymerization is characteristically limited by chain transfer processes. Since such processes are an obstacle to the synthesis of well defined structures, much effort has been devoted to exploring and understanding these processes. In the course of a copolymerization study of styrene derivatives, we have identified a strong effect of monomer structure on molecular weight which provides insight into the chain transfer processes under the particular reactions employed.

This work is concerned with ionizing radiation-initiated cationic polymerization. Such a method of initiation forms cations concurrently with unstable counterions, resulting in propagation only by free (unpaired) cations. Although fraught with experimental difficulties due to the extreme sensitivity of free cations to impurities such as water, cationic polymerization behavior in the absence of counterions has been probed extensively by various researchers. The very high propagation reactivity of free cations has been documented and the effect of monomer structure, solvent, and other reaction conditions have been explored. However, few systematic studies devoted to chain transfer processes in the absence of stable counterions have been undertaken.

Experimental

Styrene, p-CH₃styrene and p-Clstyrene (Aldrich) were washed, distilled under vacuum, stirred over calcium hydride for 48 hours, and degassed. Because of the extreme sensitivity of radiation-initiated free cationic polymerization to traces of water, the monomers were superdried by contacting with successive charges of baked out (350°C, 1 x 10⁻⁶ torr, 24 hrs) barium oxide. Benzene was treated with concentrated sulfuric acid, distilled and superdried by contacting with sodium mirrors. Monomers and solvent were vacuum transferred into calibrated tubes for volumetric measurement and then introduced into baked out (425°C, 1 x 10⁻⁷ torr, 24

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hrs) reaction flasks. Polymerizations were carried out in a Co-60 gamma-radiation source (dose rate 76,000 rads/hr), at -10°C . After irradiation the sample ampoules were opened and the polymer precipitated in methanol. Molecular weight distributions were characterized by gel permeation chromatography utilizing a Waters Linear ultrastyrigel column; samples were run at 0.25% in THF and were referenced to styrene standards.

Results

Gel permeation chromatograms for typical samples of styrene, $p\text{-CH}_3\text{styrene}$ and $p\text{-Clstyrene}$ polymerized in bulk are shown in Figures 1, 2 and 3 respectively. Molecular weight distributions are unimodal in each instance.

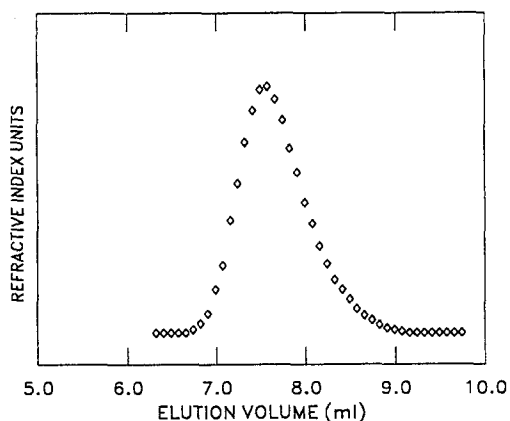


Fig. 1 Gel permeation chromatogram: radiation-initiated cationic polymerization of styrene.

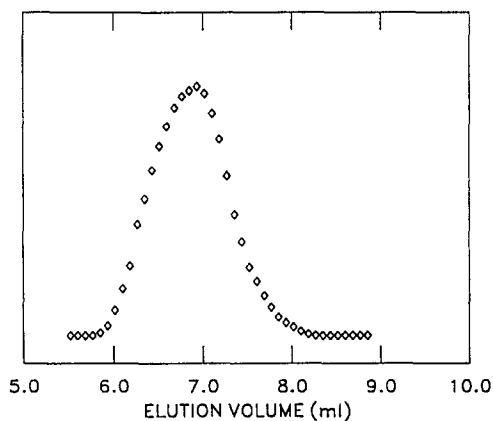


Fig. 2 Gel permeation chromatogram: radiation-initiated cationic polymerization of $p\text{-CH}_3\text{styrene}$.

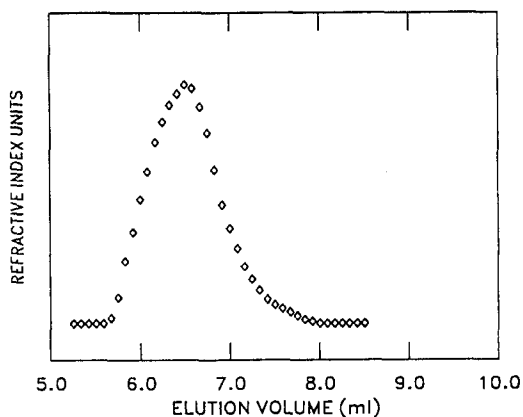


Fig. 3 Gel permeation chromatogram: radiation-initiated cationic polymerization of $p\text{-Clstyrene}$.

Number average molecular weights (M_n) and dispersion indices (D.I.) calculated from GPC data are listed in Table 1. The value of M_n shown here for styrene is in good agreement with the results of Hayashi, Williams et al. in their seminal investigation of the radiation-initiated cationic polymerization of styrene (1,2). This molecular weight is much lower than would be expected from the ratio of propagation to initiation rates (kinetic chain length) and in this bulk system must be attributed to chain transfer to monomer.

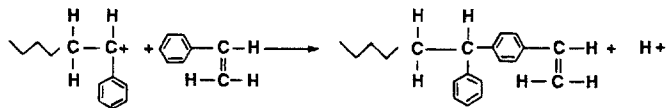
Table 1. Number average molecular weights and dispersion indices in the radiation-initiated cationic polymerization of styrene derivatives at -10°C

Monomer	Solvent	M_n	D.I.
Styrene	-	39,000	2.4
p- CH_3 styrene	-	460,000	2.6
p-Clstyrene	-	1,000,000	2.5
Styrene	Benzene	43,000	2.4
p- CH_3 styrene	Benzene	260,000	3.1
p-Clstyrene	Benzene	49,000	3.0

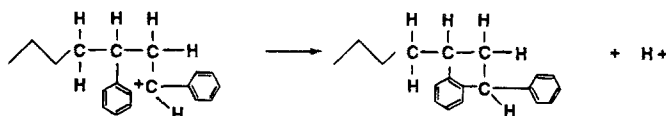
From Table 1 it is clear that much higher molecular weights, corresponding to sharply lower rates of chain transfer, are found for both p- CH_3 styrene and p-Clstyrene, with p-Clstyrene in particular exhibiting an extremely high molecular weight. Since similar propagation rates, in good agreement with the kinetic data found by Hayashi, Williams et al., were exhibited by the three monomers, it must be concluded that chain transfer processes are substantially diminished, relative to propagation, for the para substituted monomers.

Discussion

For styrenic monomers, alkylative attack on an aromatic group is thought to be the dominant chain transfer process. This may occur via attack on aromatic groups from two sources, namely monomer and polymer, as shown below.



Mechanism (1)



Mechanism (2)

Mechanism 1 involves attack on the monomer aromatic ring, while in mechanism 2 the cation attacks the penultimate aromatic ring of the propagating chain, resulting in the formation of an indane endgroup. Evidence is found in the literature for both processes (3,4).

In the present study, the differences in molecular weight in the various systems should be governed primarily by the structure of the aromatic ring under attack rather than from that of the attacking cation. This is attributed to the fact that electron donating-withdrawing cation substituents should exert similar effects in both the propagation and chain transfer reactions. Furthermore, because the presence of a monomer para substituent does not pose a steric hindrance to the propagation reaction site, the only effect of the substituent on monomer propagation reactivity should arise from its electron donating-withdrawing properties. This effect should be partially compensated by the opposite effect of the substituent on the reactivity of the cation. Thus, the similar propagation reaction rates exhibited in the three systems is quite reasonable.

In contrast, the chain transfer reaction shown as mechanism 1 may be subject to a strong steric hindrance. The most likely point of attack on the aromatic ring of a styrene molecule is at the para position (as drawn in mechanism 1), which is most accessible and is activated by the electron donating vinyl group. The presence of a para substituent makes this site inaccessible and in combination with the vinyl group poses steric hindrance to attack at any of the remaining positions. Moreover, in order to attack any of these positions the cation is forced to be in close proximity to the vinyl group, which improves the chances for attack at this location (propagation), versus attack on the ring (transfer).

A chain transfer process according to mechanism 1 thus agrees with the observed effect of monomer structure on molecular weight. The predominance of a steric effect, rather than one due to the charge delocalization ability of the substituent, would explain why the electron donating methyl group and the electron withdrawing chlorine substituent have a similar effect on the chain transfer reaction.

It would be difficult to ascribe the observed behavior to chain transfer by attack on the penultimate ring of the propagating chain. This is only likely to occur via attack at the position ortho to the main chain linkage, as drawn in mechanism 2, thus the presence of a group at the para position poses no steric hindrance. The only effect is then from the electron donating effect of the substituent, which would be opposite for the methyl and chloro groups. It is thus improbable that both the methyl and chloro groups could so strongly depress the rate of chain transfer relative to propagation if chain transfer is dominated by mechanism 2.

It is also useful to examine results found in benzene solution for these monomers. From Table 1 it is evident that the molecular weight of styrene polymerized at 20 volume percent in benzene is experimentally indistinguishable from bulk monomer samples. This suggests that chain transfer via attack on benzene is not significant at this monomer concentration, in agreement with the fact that attack on the styrene monomer aromatic ring should be more favored than attack on the unactivated benzene molecule. The molecular weight of *p*-CH₃styrene polymerized in benzene is seen to drop somewhat from that polymerized in bulk, suggesting that chain transfer by attack on benzene is significant under these conditions. Although benzene should not be as reactive toward attack by a

cation as the aromatic ring sites of p-CH₃styrene, the greater steric hindrance to attack at these sites explains why a contribution from chain transfer to benzene might be competitive.

The drop in the molecular weight of p-Clstyrene samples polymerized in benzene from that of bulk samples is striking. This again is in accord with the hypothesis detailed above; the much stronger effect of benzene in this case may reflect the greater ability of the p-Clstyryl cation to attack the unactivated benzene molecule. One other possibility should be mentioned, however, which is suggested by our findings concerning the effect of monomer structure and solvent on free cationic copolymerization behavior. We have previously reported very ordered patterns of behavior in free cationic copolymerization in dichloromethane, and have developed predictive correlations based on these findings (5). In contrast, we have found marked deviations from this behavior under certain conditions, specifically for the combination of a nonpolar/polar monomer pair copolymerized in a nonpolar solvent. These results will be proposed in a forthcoming paper to result from a strong interaction (intramolecular complexation) between the cation and the penultimate aromatic ring under these conditions. Interactions of a similar nature have been previously recognized in the cationic polymerization of styrenic monomers (6,7) as well as in vinyl ethers (8,9). Our hypothesis suggests such an interaction would be most likely with a highly reactive cation such as the p-Clstyryl cation, when polymerized in a nonpolar solvent such as benzene. Such interaction might result in a significant contribution by chain transfer by attack on the penultimate aromatic ring. It is thus difficult to say whether the effect of benzene on molecular weight in the case of p-Clstyrene polymerization is due to this or if it simply reflects the greater ability of the p-Clstyryl cation to attack benzene.

Conclusions

The results of the present study indicate that the dominant chain transfer process in the free cationic polymerization of styrene is attack on the aromatic ring of a free monomer, and that the presence of a para ring substituent greatly decreases the chain transfer process relative to propagation. In view of the increasing emphasis on controlling chain transfer so as to approach "living" cationic polymerizations (10), and the growing understanding of the important role played by the counterion in chain transfer, the use of ionizing radiation initiation to probe chain transfer processes in the absence of a stable counterion thus appears to be a quite useful approach. A more comprehensive study of the effect of monomer structure and solvent on molecular weight such processes would thus allow further insight into chain transfer processes in cationic polymerization.

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