Effect of Addition of Cations on the Simultaneous Grafting of Styrene to Rayon by Gamma–Irradiation

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Introduction

During the past ten years a number of experiments on radiation-initiated graft polymerization have been carried out for the purpose of modifying physical and chemical properties.[1] Generally speaking, preirradiation techniques[2] probably have the advantage in the production of graft copolymers, because of the formation of a smaller amount of homopolymer than when the simultaneous grafting technique is used.

However, the grafting by the latter technique sometimes takes place with a small amount of homopolymer under favorable conditions of monomer, polymer, solvent of monomer, plasticizer, and atmospheric oxygen. For example, in the rayon–styrene–methanol system, in which water[3] and atmospheric oxygen are present, the efficiency of grafting-to-monomer conversion shows high values, such as 80–90%.[4]

Grafting by this technique involves a long induction period, 90 min. or more, with ordinary radiation intensity, and this induction period seems to be owing to the oxygen involved in the polymer phase. In order to avoid this action of the oxygen, we immersed the rayon in an aqueous solution of some reducing cation, and the simultaneous grafting of styrene to rayon in the presence of air was found to be accelerated, as was expected.

Since a greater part of the aqueous solution of cation is absorbed by the rayon, this acceleration effect is characterized by the fact that the oxygen involved in the polymer phase is consumed by interaction with the cation or the radical generated by irradiation.

Experimental Procedure

The samples to be irradiated were prepared in the following way. First, 5 g. of rayon staples were immersed for 30 min. in 50 cc. of aqueous solution of $SnCl_2$, $TiCl_3$, $NiCl_2$, and other metallic salts, and then the excess solution was centrifuged off until the swelling ratio of rayon staples reached 1.8 by weight. Second, these swollen rayon staples were dipped in the solution consisting of 10 cc. of styrene and 10 cc. of methanol, which was contained in a glass tube, and then the glass tube was capped in air atmosphere. The rayon staples were an all-skin type. Monomer was purified by distillation *in vacuo*, and the other reagents were of special reagent grade.

Samples were irradiated at 23°C. by ^{60}Co gamma-rays whose radiation intensity was 3.5×10^4 r/hr.

The irradiated samples were soaked in methanol, and the mixture of polystyrene- and styrene-grafted rayon was removed, dried, and weighed (W_h).

Subsequently, homopolymer in the mixture was extracted in a Soxhlet extractor with benzene for 24 hr., and then the grafted rayon was dried at 25°C. and weighed (W_g). Thus, the amount of grafting was taken to be equal to the increase in weight (% grafting $= (W_g - W_0)/W_0 \times 100$, where W_0 is the weight of rayon), and the efficiency of grafting-to-monomer conversion was obtained from $(W_g - W_0)/(W_h - W_0) \times 100$.

Results

Acceleration of Grafting

The general forms of the grafting versus irradiation time are shown in Figure 1, at the radiation intensities of 3.5×10^4 r/hr and 2.8×10^5 r/hr. There are observed from the forms of these curves, an initial induction period of about 90 min., a steady state, an extraordinary state due to the Trommsdorff effect, and a final state in which the rate falls off as 140% grafting or 82% conversion of monomer to graft polymer is approached.

Grafting is accelerated by the addition of TiCl$_3$, SnCl$_2$, or SnCl$_4$ in a concentration of 1.0×10^{-2} mole/l. (Fig. 2) and NiCl$_2$, CrCl$_3$, or CoCl$_2$ respectively (Fig. 3), while FeCl$_2$ (Fig. 3) and KCl, Na$_2$SO$_3$, or Na$_2$S$_2$O$_3$ (Fig. 4) have little effect on acceleration. Although a considerable amount
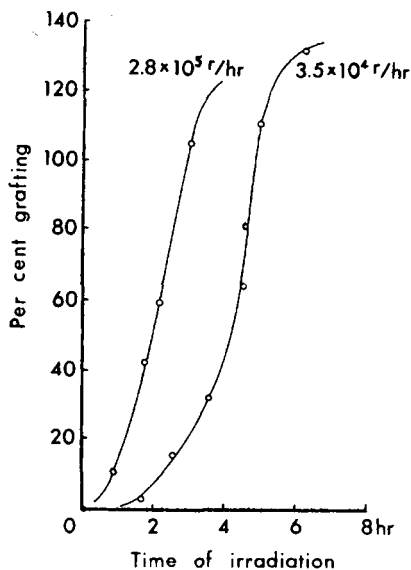

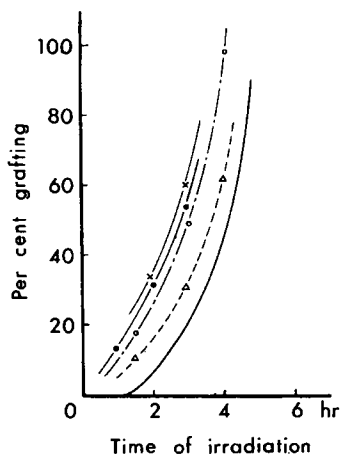
Fig. 1. Grafting vs. time curves for rayon–styrene system.

Fig. 2. Effect on grafting, of addition of: (×) TiCl₃; (●) SnCl₂; (O) SnCl₄;
(△) PbAc₂; (——) no addition of salts.

of homopolymer is formed in the case of $CuSO_4$, graft polymerization is almost inhibited also by $FeCl_3$ or $CuCl$.

The irradiation times required for the same amount of grafting (50% grafting) as in the case of no addition of salt are shortened as given below.

Salt	Time, min.
TiCl₃	80
SnCl₂	70
NiCl₂	60
SnCl₄	60
CrCl₃	50
CoCl₂	40
PbAc₂	20
FeCl₂	0–10

Since the grafting-irradiation time curves for the addition of cations run parallel to the curves for no treatment, the acceleration of grafting by cation is understood to be owing to the decrease of the induction period caused by oxygen in the polymer phase.

The efficiency of grafting-to-monomer conversion remained at 87–95% as over against 80–90% in the case of no addition of salt, when $SnCl_2$ or $TiCl_3$ was added. This fact leads essentially as a chief contribution of the radiation-generated radical in polymer to monomer conversion also in the case of no addition of salt, because the radicals formed by radiolysis of water would be scavenged by reducing cation or oxygen, but this value decreases in $FeCl_2$ to 35–55%.
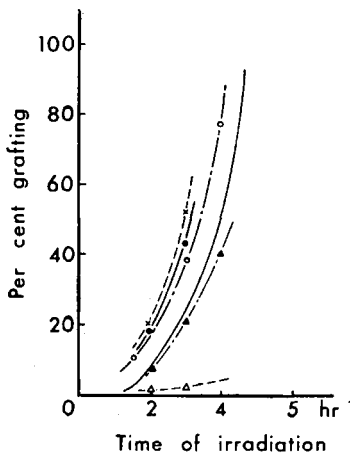
Fig. 3. Effect on grafting, of addition of: ($\times$) $NiCl_2$; ($\bullet$) $CrCl_3$; ($\bigcirc$) $CoCl_2$; ($\blacktriangle$) $FeCl_2$; ($\triangle$) $FeCl_3$, $CuSO_4$, or $CuCl$; (—) no addition of salts.
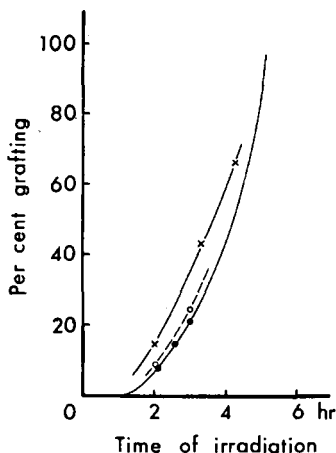
Fig. 4. Effect on grafting, of addition of: ($\bullet$) KCl; ($\times$) Na_2SO_3; ($\bigcirc$) $Na_2S_2O_3$, (—) no addition of salts.

Actually, the conversion rate of styrene monomer was below 1% grafting per hour in the same condition without rayon as graft polymerization.

Dependence of the Concentration of Stannous Chloride

To determine the effect of various concentrations of $SnCl_2$ in aqueous solution on the rate of grafting, samples were irradiated for 2 and 3 hr. Plots of per cent grafting of styrene versus the logarithm of $SnCl_2$ concentration are shown in Figure 5.

The effect of concentration of $SnCl_2$ in the range of 10^{-4} to 10^{-1} mole/l., is not so great for a 2-hr. irradiation, while the maximum is observed at a concentration of about 1×10^{-2} mole/l. for the 3-hr. irradiation. The
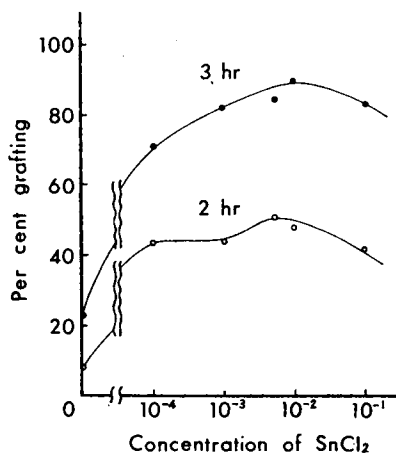
Fig. 5. Effect on grafting, of concentration, in moles/l., of SnCl₂ in aqueous solution
(irradiation time 2 and 3 hrs.).

fact that grafting is accelerated with the increase of $SnCl_2$ concentration for the 3-hr. irradiation rather than the 2-hr. may indicate that effective species to be attributed to acceleration are consumed with irradiation time.

The Effect of Variables of pH

At the concentration of 1×10^{-2} mole/l. $SnCl_2$ the grafting was carried out at various pH levels, with the addition to aqueous solution of acetic acid, hydrochloric acid, or nitric acid, and these results are shown in Figure 6.   The pH at the concentration of 1×10^{-2} mole/l. pure stannous chloride is 2.25.   The maximum of acceleration of grafting is obtained at pH 2.0,
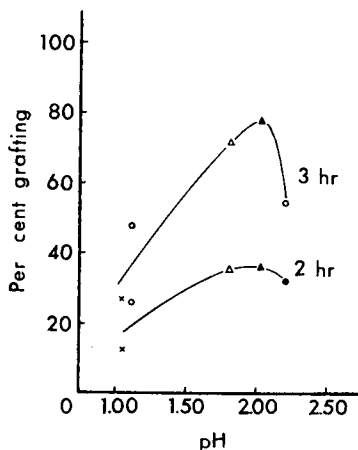

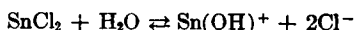
Fig. 6. Effect of pH of 0.01 mole/l. SnCl₂ solution on grafting
(irradiation time 2 and 3 hrs.).

in this case 0.6% acetic acid being added to $SnCl_2$ aqueous solution, but grafting apparently decelerates with the increase of acidity.

In dilute solution, stannous chloride hydrolyzes:

$$SnCl_2 + H_2O \rightleftarrows Sn(OH)^+ + 2Cl^-$$

Increase of acidity causes an imbalance to the left. It is reasonably assumed that the species of ion such as $Sn(OH)^+$ plays a role in the acceleration.

Discussion

It is obvious that the acceleration of grafting due to the addition of cation is caused by the decrease of the induction period, i.e., the consumption of oxygen involved in polymer phase as the results show. This effect can be discussed in connection with two things: first, the mechanism of the consumption of oxygen involved in the polymer phase by the medium of cation and, second, the oxidation or reduction reaction between cation and polymer radical.

In the first process there are two methods of consumption of oxygen, depending on whether cation or polymer is oxidized. For example, during the dosimetry, with aqueous ferrous sulfate, $G(Fe^{3+})$ has an unusually high value when organic impurity is involved. Hart[5] reported that $(G(Fe^{3+})$ is 200 under appropriate conditions of the system involving $FeSO_4$, formic acid, and oxygen, and that the rate was increased by the increase in concentration of oxygen and formic acid but was inhibited by the ferric ion.

Generally, the acceleration of oxidation of ferrous ion owing to added organic impurity may be characterized by whether RO_2 is formed. For example,

$$OH + RH = H_2O + R$$
$$R + O_2 = RO_2$$
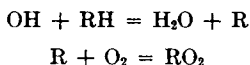
yields HO_2 by subsequent dissociation, or yields Fe^{3+} by direct reaction with Fe^{2+}.[6] In the above process, the product HCOO radical, from the reaction with OH radical, behaves as one of the chain carriers, and methanol has the possibility of acting similarly to formic acid in reducing cation solution.[8]

This impurity effect can be largely eliminated by addition of chloric ion. For this reason it is assumed that the chlorine atom formed by the reaction oxidizes Fe^{2+} more rapidly than it reacts with organic substance.

$$OH + Cl^- + H^+ = H_2O + Cl$$
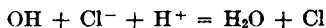
But in our system, it can be also assumed that the chlorine atom reacts with organic matter, resulting in hydrogen abstraction such as

$$RH + Cl = R + HCl$$

and this assumption would be reasonable in the case of cellulose or methanol, which are very easily oxidized. The acceleration of grafting due to $TiCl_3$ or $SnCl_2$ which are strong reducing cations agrees with the mechanism

of oxygen described above; $FeCl_2$ has no effect on acceleration because of the back reaction owing to Fe^{3+} products, or the reactivity of polymer radical toward oxidative termination by Fe^{3+}.

There are some unpublished data that titanous ion or stannous ion decomposes polymeric peroxide at room temperature and that chloric ion has little effect on acceleration of grafting.[8]

Chernova et al. reported that the high yield of oxidation of organic material was obtained in the presence of both air and ferrous sulfate.[9] This information may be susceptible to another confidence in the consumption of oxygen in polymer phase. Moreover, in the autoxidation of alkali cellulose it is found that compounds of Ni, Cr, Fe, Mn, or Co show positive catalytic action.[10] In the case of $NiCl_2$, $CrCl_3$, or $CoCl_2$ a contribution to acceleration is due to the mechanism of oxidizing polymer catalytically and eliminating oxygen rapidly, as shown above.

Collinson et al. determined that the energies of activation for the reduction of cation by polymer radical are all much smaller than that for the oxidation of titanous ion, and that in the ratio of rate constants for the reaction between cation and H or OH radical, the ferric, cupric, and ferrous ions show much smaller values than titanous ion when an aqueous solution of acrylamide involving cation was irradiated by gamma-rays.[11]

This evaluation suggests that Ti^{3+} or Sn^{2+} can hardly terminate polymer radical, and reacts with OH or HO_2 radical more rapidly than the OH radical reacts with monomer. Experimental data show good agreement with the suggestion. Actually, the efficiency of grafting to monomer conversion remained the same as when there was no addition of salt, when $SnCl_2$ of $TiCl_3$ was added, while with $FeCl_2$ or $CuSO_4$ the conversion velocity of monomer increased more rapidly, but grafting velocity decreased as compared with the case of no addition of salt.

The effect of acceleration of grafting by a reducing cation such as $TiCl_3$, $SnCl_2$, $NiCl_2$, $CoCl_2$, or $CrCl_3$ can be interpreted in terms of the three mechanisms described above, but the mechanism of acceleration by $SnCl_4$ remains obscure.

Although graft polymerization takes place in a very complicated heterogeneous system, since the greater amount of aqueous solution of cation is absorbed in polymer phase, it is sure that the mechanism of acceleration of grafting by reducing cation is closely related with a cation-mediated reaction between the radical generated by irradiation and oxygen.

References

1. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon, 1960, p. 395; A. Chapiro, "Radiation Chemistry of Polymeric Systems," (High Polymers, Vol. XV), E. Ott and M. Spurlin, Eds., Interscience, New York–London, 1962, p. 595.

2. Bouby, L., A. Chapiro, and M. Magat, *1st U.N. Conf. Atomic Energy*, Paper No. 363 (1955).

3. Chapiro, A., and V. Stannett, *Intern. J. Appl. Radiation Isotopes*, **8**, 164 (1960); I. Sakurada, T. Okada, and E. Kugo, *Isotopes Radiaticn (Tokyo)*, **2**, 296, 306, 316, 581 (1959).

4. Amemiya, A., I. Suzuki, and M. Fujimoto, *Ann. Rept. Eng. Res. Inst.*, **20** (1962).

5. Hart, E. J., *J. Am. Chem. Soc.*, **74**, 4174 (1952).

6. Allen, A. O., *The Radiation Chemistry of Water and Aqueous Solution*, Van Nostrand, New York, 1961.

7. Vermail, C., M. Cottin, and M. Haissinsky, *J. Chim. Phys.*, **49**, 437 (1952).

8. Suzuki, I., and A. Amemiya, unpublished data.

9. Chernova, A. I., V. D. Orekhov, and M. A. Proskurnin, *Proc. All-Union Conf. Radiation Chem.*, *1st* (1957).

10. Entwistle, D., E. H. Cole, and N. S. Wooding, *Textile Res. J.*, **19**, 609 (1949).

11. Collinson, E., F. S. Dainton, D. R. Smith, G. J. Thudel, and S. Tazuke, *Discussion Faraday Soc.*, **29**, 188 (1960).

Synopsis

Simultaneous radiation grafting of styrene to rayon in the presence of atmospheric oxygen was accelerated when the rayon was immersed in an aqueous solution of some reducing cation. The irradiation time required for the same amount of grafting as in the case of no addition of salt is reduced by 40 min. or more on the addition of $TiCl_3$, $SnCl_2$, $SnCl_4$, $NiCl_2$, $CrCl_3$, or $CoCl_2$, while $FeCl_2$ has little effect on acceleration. This acceleration is chiefly due to the decrease in the induction period caused by the oxygen in polymer phase. The mechanism of acceleration of grafting is discussed in relation to radiolysis of aqueous solution involving cation.

Résumé

Une radiation greffant le styrène à la rayonne en présence d'oxygène atmosphérique, était accélérée lorsque la rayonne était plongée dans une solution aqueuse contenant des cations réducteurs. Le temps d'irradiation requis pour obtenir un taux de greffage identique à celui obtenu dans le cas où il n'y a pas d'addition de sel, est réduit de 40 min. ou plus par l'addition de $TiCl_3$, $SnCl_2$, $SnCl_4$, $NiCl_2$, $CrCl_3$, ou $CoCl_2$, tandis que $FeCl_2$ a peu d'influence sur l'accélération du greffage. Cette accélération du greffage par ces cations est due principalement à la diminution de la période d'induction causée par l'oxygène dans la phase polymérique. Le mécanisme de l'accélération au greffage est discuté par rapport à la radiolyse de solutions aqueuses contenant des cations.

Zusammenfassung

Die simultane Strahlungsaufpfropfung von Styrol auf Rayon in Gegenwart von atmosphärischem Sauerstoff wurde bei Verwendung einer in eine wässrige Lösung eines reduzierenden Kations getauchten Rayonprobe beschleunigt. Die zur Erzielung eines gleichen Aufpfropfeffektes, wie im Falle ohne Salzzusatz, erforderliche Bestrahlungsdauer wird bei Zusatz von $TiCl_3$, $SnCl_2$, $SnCl_4$, $NiCl_2$, $CrCl_3$, oder $CoCl_2$ um 40 min oder mehr herabgesetzt, während $FeCl_2$ wenig Beschleunigungswirkung besitzt. Hauptsächlich wird die Beschleunigung der Aufpfropfung durch diese Kationen durch eine Herabsetzung der durch den Sauerstoff in der Polymerphase erzeugten Induktionsperiode bewirkt, Der Mechanismus der Aufpfropfbeschleunigung wurde in Beziehung zur Radiolyse wässriger Lösungen unter Beteiligung von Kationen diskutiert.