MASTER

VISCOSITY EFFECTS IN RADIATION-INDUCED

GRAFT POLYMERIZATION

by

Joseph Silverman and Ira Block

Laboratory for Radiation and Polymer Science

University of Maryland

College Park, Maryland 20742, U.S.A

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ABSTRACT

The radiation-induced grafting of styrene to polyethylene and of butadiene to poly(vinyl chloride) and to chlorinated polyethylene are examined under conditions of high matrix viscosity. The high viscosity conditions are achieved by three methods: (1) brief exposure of polymer to gaseous monomer prior to irradiation; (2) steady exposure to dilute solutions of the monomer in methanol during irradiation; (3) chemical modification to increase the elastic modulus and glass transition temperature of the polymer prior to its simultaneous exposure to monomer and radiation. With the chlorinated polymers, several viscosity-modifying effects are observed to occur spontaneously during the grafting reaction. These viscosity-related effects lead to principles of radiation-induced graft copolymerization which appear to be useful in industrial applications and in the ESR study of grafted propagating radicals.

Introduction

Although radiation-induced graft polymerization has been studied for many years, there are still many aspects relating to viscosity effects which are not completely explored. It is the purpose of this paper to discuss application of the viscosity effect in radiation-induced grafting and to discuss some of its industrial implications.

There are several published reports of what appear to be anomalous grafting effects such as increased graft yield upon dilution of the monomer, graft rates using monomer vapor that are higher than graft rates obtained with liquid monomer and graft rates that increase as the reaction temperature decreases^(1,2). Our studies of these effects show that the viscosity of the amorphous region in which the grafting occurs plays a major role. These studies have led to a practical principle for achieving high grafting yields. The yield is maximized under conditions where (1) the monomer concentration in the amorphous region is high enough to convert radicals on the polymer to propagating side chains and, (2) the viscosity of the monomer-swollen polymer system is high enough so that chain termination is inhibited, yet low enough to allow free diffusion of the monomer through the polymer.

This principle is not novel and yet it does not appear to be widely appreciated or applied. In this paper, its origins and its potential value are explored in the examination of grafting data. The discussion is concerned with the effects

of monomer concentration, crystallinity, and glass transition temperature on the polymer viscosity and grafting yield. Also some flow experiments are interpreted in terms of these concepts.

Dilution Effect

Figure 1⁽¹⁾ shows some results for the in-source grafting of styrene to low density polyethylene (LDPE) from styrene-methanol solutions. The percent graft and the equilibrium swelling are shown as a function of methanol concentration. Note that the equilibrium swelling decreases monotonically with increasing methanol content, but that the percent graft rises to a maximum at approximately 70 vol-% methanol. Some investigators have attributed the effect on grafting of methanol to its direct influence on the radical yield⁽⁴⁾ or on the conformation of the propagating radical⁽⁵⁾. It has been shown, however, that the methanol is essentially insoluble in the PE film⁽¹⁾. Thus, the effect is an indirect one in which dilution by methanol merely reduces the swelling of the film by the styrene.

This is confirmed by recent results summarized in Figure 2⁽⁶⁾. The ordinate is the percent graft after a 4-hr gamma irradiation of PE film in styrene vapor; the abscissa is the average concentration of the styrene in the film. The curve closely resembles the corresponding one in Figure 1 for grafting from methanol-styrene solutions.

The same kind of methanol effect is observed in several other systems. Figure 3⁽⁷⁾ shows the data for grafting of butadiene from methanol solution to polyvinyl chloride (PVC) and chlorinated polyethylene (PECL) as a function of methanol

concentration. Again, the graft yield increases upon dilution of the monomer to a maximum at approximately 75 vol-% methanol. In the grafting of butadiene to LDPE the graft yield remains constant upon dilution of the monomer to approximately 80 vol-% methanol and decreases as the monomer is diluted further. In each case, the principal effect of the alcohol is its influence on the monomer concentration in the polymer.

These data show that the monomer acts in two competing ways: (1) monomer concentration is associated with an increase in the viscosity of the amorphous region, as shown by an increase in the elastic modulus, which inhibits the termination of growing radicals more effectively than their propagation and, thus, enhances grafting; and (2) a lowered monomer concentration reduces the propagation rate, and by increasing the viscosity, reduces transport of monomer from the solution to the polymer, thus, diminishing grafting.

The proposed explanation has been confirmed by measurements of in-source and post-irradiation kinetics. In-source grafting under conditions that apply at the maxima of Figures 1 and 2 give weight gains that increase with the 1.43 power of time when grafting with liquid monomer solutions and quadratically with time when grafting with styrene vapor. There is also a large post effect in both cases. An unexpected result of these studies is the fact that polyethylene swollen with 5 wt-% styrene is a

high viscosity medium as far as grafting is concerned despite the fact that it is at least 50°C above its glass transition temperature (T_g). The results are consistent with the view that the grafting is due to long-lived radicals propagating under conditions of strongly inhibited termination. Confirmatory ESR evidence has been obtained with the butadiene-PVC system where a long-lived propagating radical (lifetime ~ 2 min) is observed at room temperature until a 3% graft is achieved; above this level, the grafted polymer becomes less rigid and the associated decrease in viscosity gives rise to a much shorter-lived radical.

Crystallinity

One of the more interesting observations in grafting kinetics is that the grafting rate to polyolefins increases with increasing crystalline content of the polymer^(8,9). This is surprising at first glance since the grafting takes place primarily in the amorphous region.

We have observed this effect in the grafting of styrene to LDPE, high density polyethylene (HDPE) amorphous ethylene-propylene copolymer (EP) and in the grafting of butadiene to PECL films. In the latter set of experiments measurements were made on samples having the same chlorine content in the amorphous region but differing in crystalline content as determined by infrared analysis. As shown in Table 1, the graft yield increases with crystalline content.

This effect is consistent with the view that a higher viscosity in the amorphous region is associated with greater crystallinity. Of course, high crystallinity is not a requisite for high viscosity. In the case of amorphous PVC, the viscosity at room temperature is high because the polymer is well below its T_g .

Elastic Modulus

Since the viscosity of the amorphous region of a polymer is difficult to determine, it is useful to analyze grafting kinetics in terms of related physical properties which are more easily measured. The elastic modulus (E) is a property related to viscosity of the polymer, and it has served as the basis of the analysis of the work by Takamatsu and Shinohara on the grafting of styrene to PVC⁽²⁾.

They measured the graft rates and the modulus of monomer-swollen films as a function of absorbed monomer concentration. They observed that the grafting rate is a maximum when the absorbed styrene concentration is 3.2 molar. (The saturation concentration is 5 molar). E was found to be constant at concentrations up to 3.2 molar. Beyond that, the modulus decreased linearly with increasing styrene concentration while the graft rate decreased. They ascribed their results to a decrease in the termination rate constant as the monomer concentration was decreased.

We have made related studies on the grafting of butadiene to PECL films as a function of chlorine content. In these systems,

the solubility of monomer in the films and the radical yields are almost independent of chlorine content. Using the work of Oswald and Kubu⁽¹¹⁾ to obtain the elastic moduli of the original films, we found a linear relationship between graft yield and E up to a value of $\sim 10^6$ g/cm²; as E was increased beyond this point by further chlorination, the graft yield remained constant. The results are shown in Figure 4.

The above observations are consistent with our view of the role of matrix viscosity in grafting kinetics. For low viscosity systems the graft yield rises with increasing modulus due to inhibition of the termination reaction. When the matrix viscosity becomes very high the propagation reaction is also inhibited and increasing viscosity no longer increases the graft rate.

Glass Transition Temperature

Another measurable property related to viscosity is the difference between the reaction temperature (T) and T_g . The work of Schamberg and Hoigné⁽³⁾ and our experiments on grafting reactions near the glass transition temperature illustrate the concepts involved. Schamberg and Hoigné measured grafting rates of a variety of monomers to several polymers as a function of temperature near the T_g of the dry polymer. They found in each case that the graft yield was a maximum at the T_g of the dry polymer. In our work, we obtained the T_g of the chlorinated polyethylene films as a function of chlorine content from the data of Oswald and Kubu⁽¹¹⁾, and plotted $(T - T_g)$ against the

yield of the grafting reaction between liquid butadiene and the PECL films (Figure 5). It was found that as the T_g of the dry polymer was raised to the reaction temperature ($T = 23^\circ\text{C}$) the graft yield increased, reaching a limiting value for $T_g \geq T$.

It is noteworthy that this useful correlation between maximum graft yield and T_g is made using the T_g of the dry polymer, and not the T_g of the monomer-swollen polymer. This seems to be a fortuitous coincidence. Since the T_g of the dry polymer is greater than that of the monomer-swollen polymer the viscosity of the reaction system is lessened. It appears that the increase in termination rate is either trivial or is overwhelmed by the effect of the increased rate of monomer diffusion.

Flow Experiments

The practical merit of grafting under conditions of high matrix viscosity is illustrated by measurements performed on the grafting of gaseous butadiene to PVC powder.

The grafting was carried out by flowing the gaseous monomer through a packed bed of powdered polymer. Grafting rates were determined from measurements of inlet and outlet flow rates. The bed was first equilibrated with the flowing gas after which the gamma source was lowered near the reactor.

The results are summarized in Figure 6. The rate of monomer consumption rises to a maximum and then falls to a

steady state value which is independent of dose rate. The effect of decreasing the dose rate is to lower the maximum and to increase the time required to reach it.

These results confirm and extend the earlier work of Sagane and co-workers^(12,13) on the same system. Both sets of results are consistent with the following explanation. The polymer initially contains a small amount of absorbed monomer (1.5%) and the viscosity of the grafting medium is high. In the early stages of the irradiation the grafting rate is approximately proportional to the square of time. This comes about because (1) the radical population increases almost linearly with time since recombination of the radicals is inhibited by the rigid matrix, and (2) the flux of monomer into the polymer increases. The latter occurrence is due to the fact that the reaction rate is greater than the initial diffusion rate and the grafting medium becomes depleted in monomer. Still in the interval before the maximum is reached, the monomer flux into the polymer sustains the reaction rate at a high level. As the copolymer builds up in the matrix and the solubility of monomer increases, the polymer is plasticized and the viscosity falls. Near the point where the maximum is reached the viscosity becomes low enough for the termination reaction to become important and the reaction rate decreases. The reaction rate continues to fall until the

rate of consumption of monomer equals the rate of supply. Under these steady-state conditions where the monomer concentration (2.5%) is low, and therefore the viscosity is low, the reaction rate is controlled by diffusion of monomer. Thus, most of the primary radicals are lost by recombination processes prior to initiating graft chains, and the graft rate is independent of dose rate.

Figure 7 shows measurements of the grafting rate versus time with (solid line) and without (dashed line) irradiation. Note that if irradiation ceases prior to the attainment of the maximum, the graft rate continues to rise for some time. However, if irradiation ceases after the peak has been passed the grafting rate decreases. This shows that in the early stages of the reaction the matrix is so viscous that radical termination is completely inhibited. Whereas after the production of a small amount of copolymer (about 3%) the viscosity of the matrix has been reduced so that the termination reaction is important.

Closely related to these flow experiments are the following batch experiments on the grafting of liquid butadiene to PVC films.

Figure 8 shows the results for irradiation times up to 10 hours at dose rates from 3 to 340 krad/hr⁽⁷⁾. In all cases there is an initial period during which the grafting rate has a relatively high value, and after which it decreases to a constant value. The transition period lasts from two to four hours, de-

pending on dose rate. Of particular significance is the result that it is during the transition period that most of the grafting occurs, e.g., at 340 krad/hr one obtains 5% graft in the first hour but only 10% graft after 10 hours. Following the transient, a steady-state condition is reached at which the reaction rate is constant at 0.45% per hour at dose rates greater than 10^4 rad/hr. At lower dose rates the steady-state grafting rate decreases with decreasing dose rate and the contribution of the graft during the transient period to the total graft decreases. These results fit the mechanism advanced above.

The salient features of the above results are that (1) under conditions of low monomer concentration and high matrix viscosity chain termination is greatly hindered, and (2) grafting rates under these conditions are far higher than in the case of high monomer concentration and low matrix viscosity. In addition, homopolymer production is greatly reduced. We have, for example, found no ether-extractable homopolymer when grafting butadiene to PVC from 75 vol-% methanol solution. Similarly the benzene-extractable homopolymer obtained from PE-styrene grafts produced under high viscosity conditions is also very small⁽²⁾.

Applications

Grafting under conditions of low monomer concentration and inhibited termination can be the basis of useful scientific and industrial applications. It can permit post-irradiation

examination of propagating grafted radicals by ESR; this technique has been applied successfully at this laboratory to several systems. In addition, it can be the basis of efficient post-irradiation grafting processes. Grafting to polymers that have been preirradiated in the absence of monomer is wasteful in radiation energy, since almost all of the primary radicals formed disappear by bimolecular recombination before the irradiated polymer is exposed to monomer. If the polymer is swollen with a small concentration of monomer the primary radicals produced by ionizing radiation can be efficiently converted to propagating side chains which live long enough to continue propagation to a desired yield even when the grafting system is removed from the radiation field.

In the ideal case, the partially swollen polymer is given a short exposure to a high dose rate source and is then transferred to a reaction vessel containing monomer. This would provide a high radiation yield at a high through-put (in the radiation field). This is to be contrasted with completely swollen polymers where the high mobility of the radicals could effectively eliminate the possibility of practical post-irradiation grafting applications. Also it is superior to stationary-state grafting methods which can only provide high radiation yield at low production rates or high production rates at a high radiation energy cost.

The role of viscosity and related physical properties is well known to polymer chemists. It is also known to be important in several radiation-induced polymerization processes of practical interest. Still earlier works^(2,13,14) which contain many of the

concepts cited in this paper are not widely appreciated, and the concepts themselves are not systematically applied in grafting systems. We recommend their further study and widespread application.

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TABLE I

Effect of Crystal Content on Graft
Yield of Butadiene to Chlorinated Polyethylene

PCA*	Crystal Fraction	Graft ⁺ Yield (wt-%)
25	0.22	4.8
25	0.30	5.8
25	0.38	7.7
53	0.16	6.9
50	0.22	8.4
55	0.26	9.4

* PCA is defined as the percent chlorine added to the amorphous region of the polymer.

⁺ Irradiation time = 5 hr
Dose rate = 0.34 Mrad/hr

Fig.1, Plots of (o) amounts of graft for 3 hr and (□) equilibrium swelling of polyethylene versus methanol concentration in outside styrene methanol solution. Grafting at 20°C and 9.5×10^4 rad/hr; swelling at 25°C.

Fig. 2, Effect of swelling of polyethylene by exposure to styrene vapor on graft rate. Polymer irradiated in monomer vapor at 20°C and 1.98×10^4 rad/hr. Width of Horizontal line is range of monomer concentration during experiment.

Fig.3, Percent Graft Yield to LDPE, PECL, and PVC from BD-Methanol Solution. Polymer Irradiated in Monomer Solution for 5 hr at Room Temperature. ● PCA=45; ■ PVC; □ PCA=25; ○ LDPE

Fig. 4, Percent Graft to PECL versus Elastic Modulus of Polymer. Dose Rate =
● 340 krad/hr; and ■ 60 krad/hr. Polymer Irradiated 5 hr at Room
Temperature in Liquid Monomer. Inset = Expanded Scale.

Fig. 5, Percent Graft to PECL as a Function of the Difference Between the Reaction Temperature and the T_g of the Polymer. Dose Rate = ● 340 krad/hr; ■ 60 krad/hr. Irradiation time = 5 hr. $T = 23^\circ\text{C}$

Fig. 6, Grafting Rate of Butadiene to PVC Powder Vs. Time, Temperature 23°C
Gas Flow Rate = 15 cc/min.----wet, —dry Gas.

Fig. 7, Post Irradiation Grafting in the Butadiene Vapor-PVC Powder System

Dose Rate = 8×10^4 r/hr, Temperature = 20°C

— Continuous Irradiation ---- Post Irradiation

Fig. 8, Percent Graft to PVC versus Irradiation Time. Polymer Irradiated in Liquid Monomer at Room Temperature. Dose Rate = $\circ$ 340 krad/hr; $\square$ 60 krad/hr; $\bullet$ 10 krad/hr; and $\blacksquare$ 3 krad/hr

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