Molecular Weights of Grafted Polystyrene onto γ-Preirradiated Cellulose Diacetate

STELIO MUNARI, G. CARLO TEALDO, GIACOMO CANEPA, and
CORRADO ROSSI, *Istituto di Chimica Industriale,*
Università di Genova, Italy

Synopsis

The behavior of molecular weights of grafted polystyrene onto γ-preirradiated cellulose diacetate was studied. The grafting of styrene onto cellulose diacetate was kinetically followed with particular attention paid to the polystyrene molecular weight behavior. The molecular weight was evaluated with the polymer fractions obtained by acid hydrolysis of the grafted copolymer. From the experimental results it appeared that the grafted chain molecular weight is completely controlled by the physical properties of the polymeric matrix either during a "bulk" or a "front" grafting.

INTRODUCTION

A valid interpretation of the mechanism by which a grafting reaction takes place can be obtained only through an analysis of molecular weight of the grafted chains. It is obviously clear that this analysis can be more easily achieved with a system allowing a quantitative separation of the grafted chains from the polymeric matrix. It is well known[1–8] that a system which allows this separation to be achieved is styrene grafted onto cellulose diacetate; indeed in such a copolymer the polymeric matrix (CDA) can be destroyed by acid hydrolysis. Most of the work on this system has been accomplished employing the simultaneous irradiation technique and using solvents as swelling agents. This work was carried out in bulk to avoid complications of chain transfer to solvent[9] and a vacuum preirradiation technique to prevent formation of homopolymer due to the irradiation. It is also known that styrene monomer practically does not swell CDA and therefore such a grafting system, in the absence of swelling solvents, proceeds with a frontal mechanism similar to the one found for other systems previously studied.[10–13]

EXPERIMENTAL

The cellulose diacetate (CDA) powder was purchased through Fluka. The substitution degree was 2.07 and the average molecular weight about 6×10^4 according to the relation: $[\eta] = 1.49 \times 10^{-2} M^{0.82}$ at 25°C in acetone. The films, 0.1 ± 0.02 mm thick, were made by very slow evaporation in dry

atmosphere from an acetone solution. The polymer (about 1 g) was irradiated by a ^{60}Co source with a dose rate of 24,000 rad/hr, at room temperature. Styrene monomer, twice distilled before use, was added to irradiated films, following a conventional experimental technique previously described.[11,12] The grafted films were washed first in cold benzene to extract the outer homopolymer, then in hot benzene by prolonged Soxhlet extraction. The yield was calculated by weight increase using the well-known relationship

$$\frac{P - P_0}{P_0} \times 100$$

where P = final weight and P_0 = initial weight.

The obtained copolymer was then dissolved in an acetone–methylene chloride (50:50 v/v) mixture and subsequent hydrolysis was carried out for 24 hr in boiling $3N$ HCl. The grafted polystyrene was isolated and purified by successive dissolutions in benzene and precipitations in methanol. Polystyrene samples examined by infrared spectroscopy showed no characteristic absorption of the CDA. Blanks showed that no change in the polystyrene molecular weight occurred during the hydrolysis process. In Table I it is shown that the method used allowed a nearly quantitative recovery of the grafted polystyrene.

TABLE I

Polystyrene grafted, g	$\dfrac{P - P_0}{P_0} \times 100$	Polystyrene recovered after hydrolysis, g	Polystyrene recovered, %
0.0751	6.5	0.0727	96.8
0.1208	11.05	0.1192	98.6
0.1289	12.1	0.1248	97.4
0.2833	22.1	0.2720	96.0

The polystyrene molecular weight M was calculated from the relationship

$$[\eta] = 11.3 \times 10^{-5} M^{0.75}$$

at 25°C in benzene.

Several runs carried out with a styrene–methylene chloride mixture allowed us to evaluate the molecular weights of the grafted polymers obtained in the presence of a matrix-swelling agent.

RESULTS AND DISCUSSION

The grafting of bulk styrene onto irradiated CDA, due to the very low swelling, initially occurs in the outer layers of the polymeric matrix, then it proceeds to the inner layers when the formed copolymer allows further penetration of the monomer. This grafting mechanism, previously in-

vestigated by us[11,12] and others,[14] has been defined as grafting by "front mechanism." On the other hand, with a solvent–monomer mixture able to swell the polymeric matrix, the grafting occurs, from the beginning, not only at the surface but also in the inner part of the polymer by a mechanism which has been defined as "grafting in bulk."[12,13] This behavior can be clearly shown by microdensitometric measurements of microscopic sections.
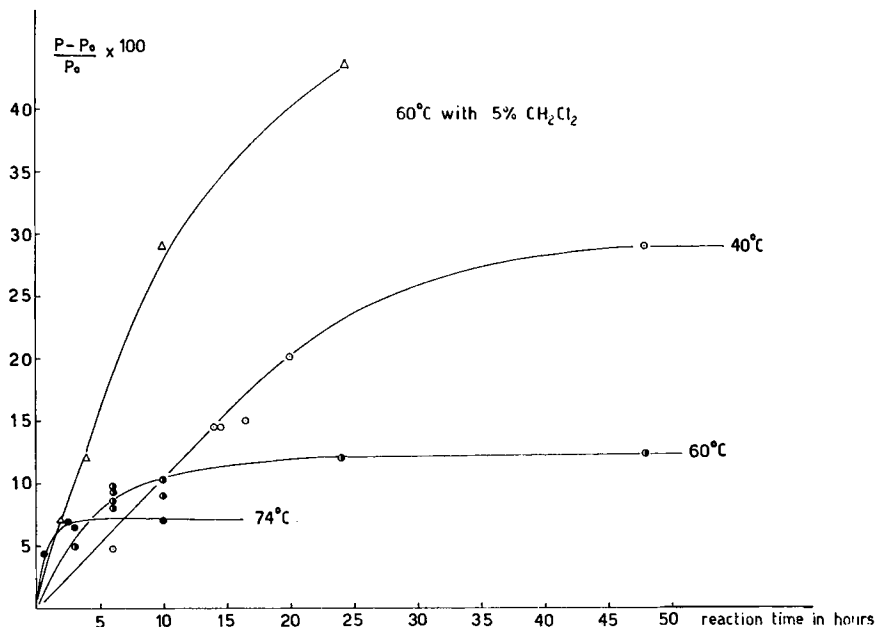

Fig. 1. Grafting yield versus polymerization time in hours for the CDA–styrene and CDA–styrene–methylene chloride mixture systems. Polymerization temperatures 40°C, 60°C and 74°C; radiation dose 0.3 Mrad.

The overall behavior of the yields in the system CDA–styrene is shown in Figure 1. As may be expected, the yields increase by lowering the reaction temperature. The upper curve in the same plot refers to a styrene–methylene chloride mixture containing 5% by volume of CH_2Cl_2. Keeping the other experimental parameters constant, the solvent addition greatly increases the yields.

The choice of this solvent was based on the following considerations: (a) the high swelling properties of this solvent toward CDA, as shown in Figure 2, in which the swelling of CDA films as function of the amount of CH_2Cl_2

TABLE II

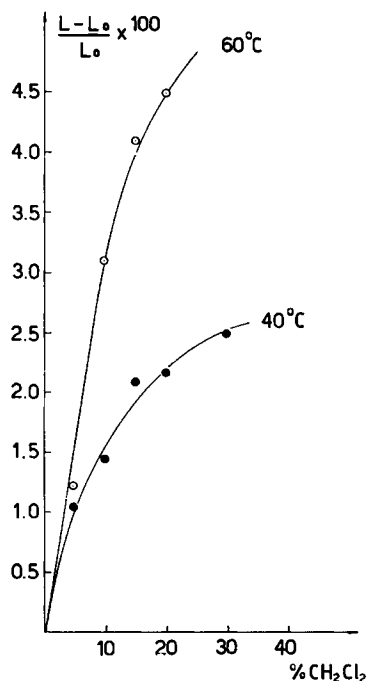| Reaction time, hr	MW of inner homopolymer	MW of thermal homopolymer	MW of grafted polystyrene
6	0.2×10^6	1.8×10^6	0.19×10^6
24	0.195×10^6	1.7×10^6	0.22×10^6

Fig. 2. Swelling of CDA films with styrene–methylene chloride mixtures. L_0 = initial length of CDA film; L = length of film after contact with styrene–methylene chloride mixtures. Contact time 30 min.

in styrene–CH_2Cl_2 mixtures is reported, allowed us to use low amounts of solvent, and therefore the dilution effect can be neglected; (b) has been shown by several workers,[9,15] the grafted chain molecular weight can be strongly affected by chain transfer, depending on the characteristic transfer constant of the solvent. It is known that the chain transfer constant of methylene chloride has the relatively low value of 0.15.[16] Therefore, in the concentration range used, chain transfer has no practical effect on the molecular weight.

In Figure 3 the molecular weight behavior of the grafted chains is plotted as a function of the grafting time. There is a net increase in the earlier stages of the reaction, after which a constant value is obtained. Although increasing the temperature has the expected effect of lowering the molecular weight, the molecular weights obtained in the earlier stages of the reaction are very similar. We believe that this latter phenomenon can

TABLE III

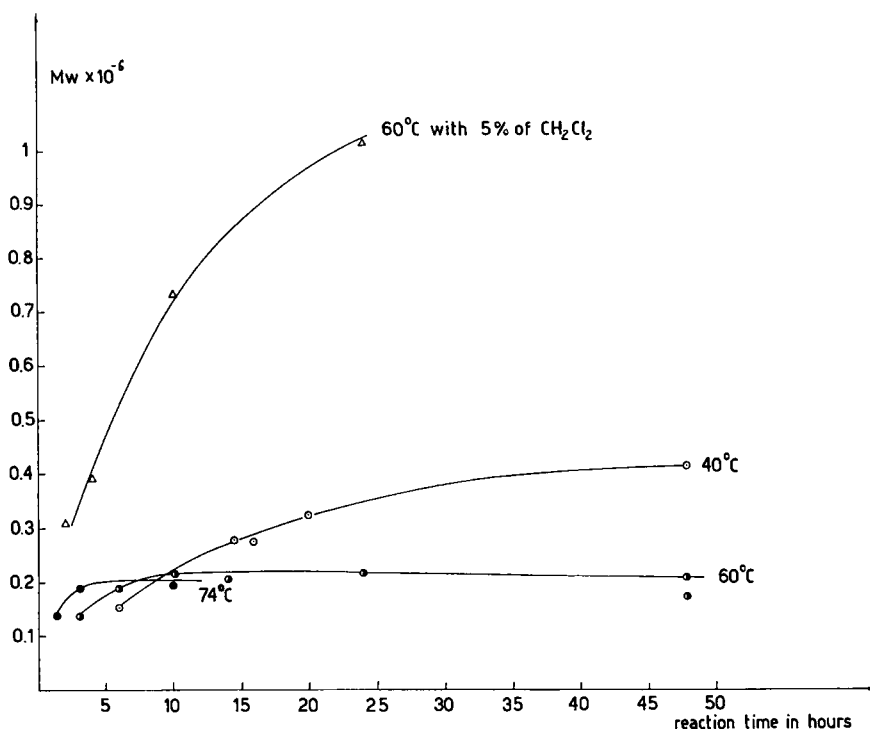| Reaction time, hr	MW of inner homopolymer	MW of grafted polystyrene
4	0.39×10^6	0.38×10^6
24	0.99×10^6	1.02×10^6

Fig. 3. Average molecular weights of grafted polystyrene versus polymerization time for CDA–styrene and CDA–styrene–methylene chloride mixture systems. Polymerization temperatures 40°C, 60°C, and 74°C; dose 0.3 Mrad.

be strictly related to the availability of the monomer inside the polymeric matrix and that the monomer availability depends on the behavior of the backbone in respect to the monomer used.

The molecular weight increase with time both with bulk monomer and monomer–solvent mixtures may be dependent on several phenomena: (a) lower concentration of free radicals in the polymeric matrix as the reaction proceeds; (b) impurities that can be active as chain ends, and whose concentration decreases with time, since they can be taken out from the matrix to the surrounding medium; (c) higher concentration of monomer in the matrix with time related to higher swelling of the grafted copolymer; (d) decrease of chain termination due to the fact that the grafting at the beginning takes place in the accessible i.e., amorphous regions of the matrix and, as the reaction time goes on, can take place also in the more crystalline regions.

From Figure 3 it also appears that the molecular weights of the grafted chains, when the methylene chloride is added to the reaction mixture, are higher than those obtained using bulk styrene. This increase depends on the different environmental condition of the matrix depending on the absence or presence of the swelling agent. Indeed, in a system in which
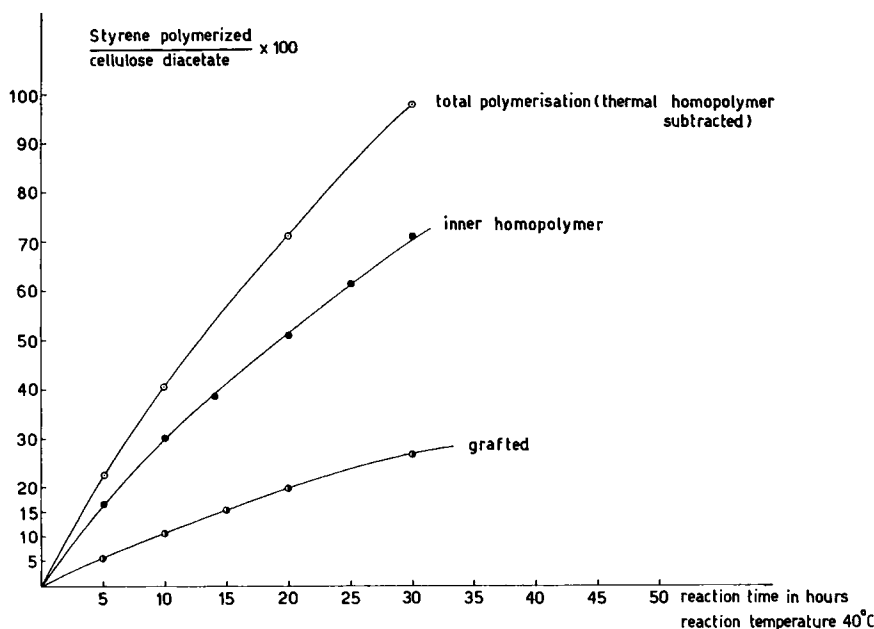
Fig. 4. Percentage of polystyrene formed versus polymerization time. Grafting temperature 40°C.

the reaction takes place by "fronts" there is a starvation of monomer as it can diffuse only through the previously grafted layers. Moreover, the grafted chains are growing in a very rigid medium, therefore, coupling scarcely can occur, but the termination takes place mainly by transfer. In practice this fact leads to an increase of inner homopolymer. In the case of the bulk grafting, due to backbone swelling, the monomer diffusion is enhanced and consequently the yield in grafted polymer is increased. In order to explain in this case the increase of the molecular weight with reaction time, the same reasoning as in the "front" mechanism can be invoked.

We also carried out some measurements in order to investigate the molecular weight behavior of the inner homopolymer. As previously mentioned, both in the presence and absence of solvent, a certain amount of inner homopolymer is formed. The amount of this inner homopolymer is higher when the reaction takes place by the "front mechanism" then by the "bulk mechanism." This phenomenon was ascertained in previous work by us.[12] A feature contributing to the presence of inner homopolymer, as confirmed by the dilatometric measurements reported in Figure 4, could be the decomposition of hydroperoxides during the polymerization reaction due to residual traces of oxygen present in the matrix during irradiation.

In Table II are reported the molecular weights of samples of inner homopolymer obtained using bulk styrene. It is interesting to note that the molecular weight of this inner homopolymer is of the same order of magni-
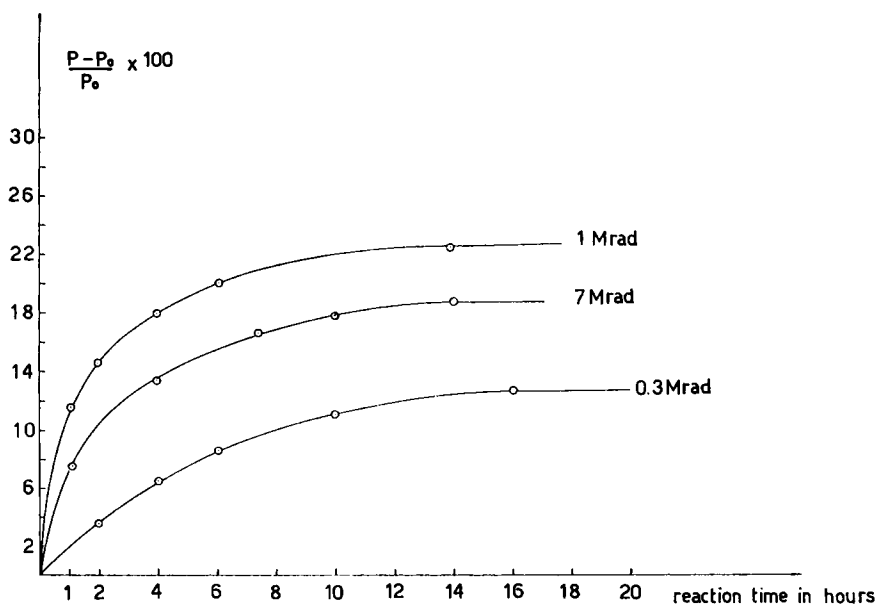
Fig. 5. Grafting yield versus polymerization time at 60°C. Doses 0.3 Mrad, 1 Mrad, and 7 Mrad.

tude as grafted polystyrene and smaller than that of external thermal polystyrene. The similar range of the molecular weight shown by inner homopolymer and grafted polystyrene indicates that the process is completely controlled during the propagation and termination steps by the physical properties of the matrix. This also means that the grafting bond to the matrix does not play an important role in controlling the molecular weight.

The same phenomenon takes place when a solvent is added to the reaction mixtures. This result is shown in Table III. The ratio inner homopolymer/grafted polymer in the presence of a solvent is less than in the case of a reaction carried out in a pure monomer. The lower yield of inner homopolymer, in this case, could be partly explained in terms of a coupling reaction between two growing chains. However, as the reaction takes place in a very viscous medium, we believe that this effect could be enhanced by the lowering of the K_t due to the solvent and by the presence of some unextractable high molecular weight homopolymer.

The behavior of the yields and of the molecular weight as a function of the total dose absorbed is reported in Figures 5 and 6. Higher yields are initially obtained on increasing the dose, but for very high doses (7 Mrad) the apparent yields decrease. This effect is strongly dependent on the irradiated CDA degradation as has been clearly demonstrated by Wellons and co-workers.[6] From their experimental results it appeared that the number of cleavages was higher than the number of the grafting centers and a certain amount of the grafted copolymer can be lost due to the fact that

it can be either extracted during the grafting reaction into the surrounding medium or during the subsequent extraction with benzene.

This phenomenon has also been confirmed by us by infrared spectroscopy. The analysis has shown that with samples submitted to severe irradiation doses, the extracted polystyrene carried amounts of CDA. This effect can also be of some importance at very high grafting yields; in fact, under these conditions the matrix can collapse. Moreover, it cannot be neglected that the molecular weight of grafted chains is several times higher than the
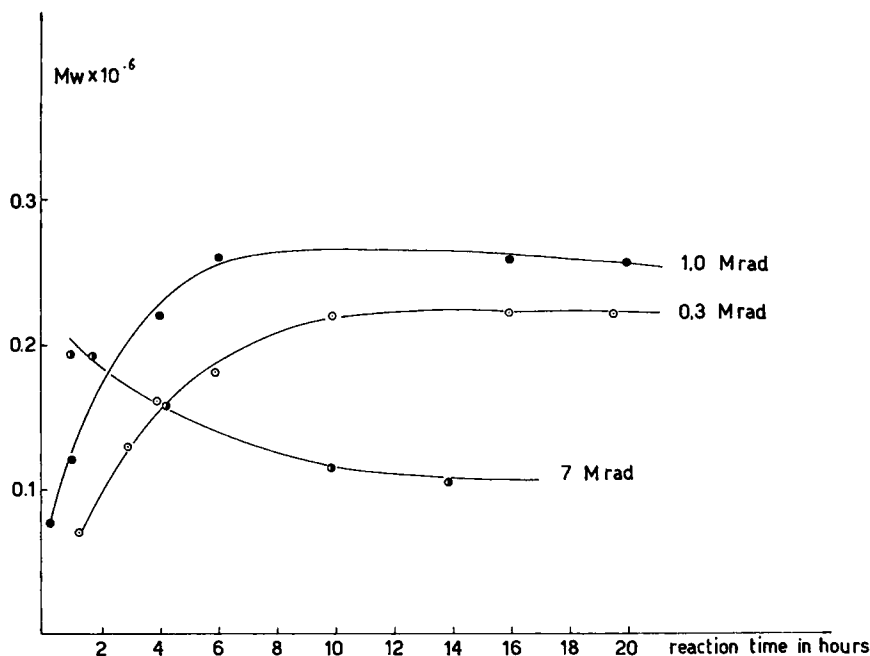

Fig. 6. Average molecular weights versus polymerization time at 60°C. Doses 0.3 Mrad, 1 Mrad, and 7 Mrad.

molecular weight of the matrix. The change in the swelling properties in benzene of the grafted matrix is reported in Figure 7. If a certain amount of the grafted chains is lost, obviously the molecular weight evaluation is completely altered. Due to the above mentioned phenomena we will loose especially the higher molecular weight chains and those grafted onto CDA radiolyzed fragments. The plot in Figure 6 clearly shows this behavior. The apparent molecular weight of the grafted polystyrene for the highly irradiated samples (7 Mrad) decreases with the reaction time.

At 1 Mrad the molecular weight of the grafted chains is higher than that obtained at 0.3 Mrad. It is difficult to establish to what phenomena this increase can be attributed: (a) higher coupling due to the increase in radical concentration; (b) higher swelling of the matrix due to the radiolytic deg-
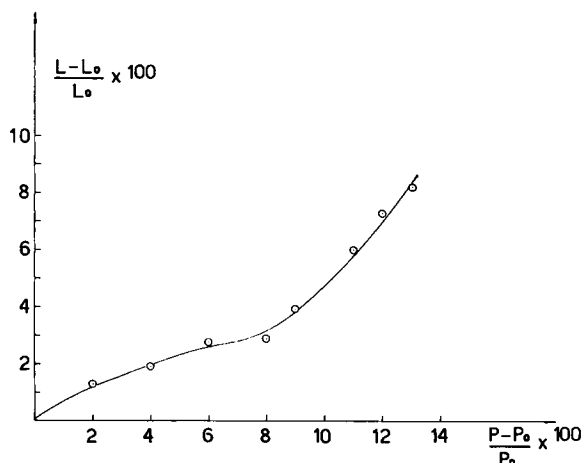
Fig. 7. Swelling of grafted copolymer (styrene onto CDA) in benzene at 60°C. $L =$ Initial length of CDA–styrene copolymer film; $L_0 =$ final length of CDA–styrene copolymer film after contact with benzene at 60°C.

radation; or (c) higher swelling due to the larger yield rates. In our opinion, the coupling contribution must be quite low.

In spite of the fact that a more precise evaluation of molecular weight could be obtained by means of number-average molecular weight determination, from our experimental data the following considerations can be drawn:

(a) The grafted chain molecular weight is completely controlled by the physical properties of the polymeric matrix and this fact is confirmed by the values obtained in the two different ways in which the grafting has been carried out—by "fronts" and in "bulk."

(b) The inner homopolymer molecular weight is always of the same order of magnitude as the grafted one; it is therefore strictly dependent on the matrix conditions.

(c) The molecular weight increases with the reaction time up to a limiting value, and from the ratio between yields and its molecular weight it appears that most of the active sites react in the initial stage of the grafting. The increase of the yields with time can be attributed to a very small number of high molecular weight chains located in the more inaccessible regions of the network.

(d) At high irradiation doses, mainly due to radiolytic damage, a certain amount of the grafted copolymer is lost both during the grafting reaction and during the subsequent extraction with solvents.

These factors make a quantitative kinetic treatment virtually impossible. In the present system these difficulties are enhanced by the high rate at which the radiolytic damage occurs.

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