Grafting of Vinyl Acetate onto Poly(vinyl Chloride) in Solution

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Synopsis

Radiation-induced grafting of vinyl acetate (VAc) onto poly(vinyl chloride) (PVC) was performed in solution with dimethylformamide (DMF). Grafting was studied as a function of dose, dose rate, and VAc/PVC ratio. The amount of grafting was measured by IR spectroscopy on the graft copolymer fraction insoluble in hot methanol. The homopolymerization of VAc was also studied in the same conditions, in order to check the influence of the solvent on radiochemical reactions leading to graft copolymers. The results show that the grafting can be easily obtained and the graft copolymer will be tested for the preparation of ultrafiltration membranes.

INTRODUCTION

As is well known, it is possible to induce new chemical and physical properties in a polymer by grafting the adequate monomer on it. This technique is therefore applicable in the field of textiles and technopolymers, with the purpose of obtaining new products suitable for industrial applications. Many people have then devoted themselves[1-3] to the study of the grafting of various monomers onto several polymers. Recently a lot of work has been done regarding the grafting of poly(vinyl chloride) (PVC).[1-10] Several monomers were used: acrylic acid, methyl methacrylate, acrylonitrile, vinylpyridine, styrene, vinyl acetate and the methods used to obtain grafting ranged from chemical[1,2,8,9] to radiochemical[1-7,10,11] ones. In most cases it was decided to perform the grafting reaction with the polymer in the solid state and liquid monomers.[1-11] PVC solvents were also used[6,8] but sometimes as swelling agents,[12] in order to increase the amount of grafting, and to regulate the length of the side chains. As expected, such graft copolymers show chemical characteristics of both the matrix and the grafted monomer. In most cases they are therefore soluble in a wider range of solvents than the PVC alone. This can be very useful when particular kinds of solutions are needed as, for example, in the preparation of asymmetric membranes.[13,14]

With these outlooks in mind, we started our work with the aim of obtaining the grafting of vinyl acetate (VAc) onto PVC directly in the liquid phase, that is dissolved in dimethylformamide (DMF), and studying some kinetic features of the reaction.

EXPERIMENTAL

Materials

Our experimental tests were performed using the following materials: dimethylformamide (DMF) by Hoechst was accurately dried by treatment with

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molecular sieves; Vinyl acetate (VAc) by Fluka was purified and freed from the stabilizer (hydroquinone) by vacuum distillation. The pure monomer was then stored at −20°C. Poly(vinyl chloride) (PVC) supplied by Hoechst; purity more than 99.9%; M_w = 120,000. Methanol, reagent grade by Hoechst; tetrahydrofuran (THF), reagent grade by Hoechst.

Experimental Technique

The reaction of grafting was carried out according to the following procedure: The PVC was dissolved at room temperature into dry DMF to obtain clear solutions having 100 g/dm^3 of polymer and dynamic viscosity of 60 CPs at 20°C. Pure VAc monomer was then added in order to reach concentrations ranging between 20 and 60% by volume. These mixtures were used to perform the grafting reaction, while solutions of VAc alone in DMF were employed to analyze the homopolymerization kinetics. The solutions were placed into glass vials as the one schematized in Figure 1, and then vacuum degassed through several cycles of freezing at liquid nitrogen temperature, followed by melting under vacuum, at room temperature.

When no more gas bubbles were released from the liquid, the vials were flame sealed and submitted to irradiation from a Co^{60} gamma rays source. The dose rate ranged between 0.168 Gy/min and 1.92 Gy/min; the dose absorbed ranged from 230 to 15,300 Gy in the case of homopolymerization, and from 230 to 2700 Gy in the case of the grafting tests.

After irradiation, the vials were opened and poured into water in order to precipitate the polymers (homo and graft). The obtained solid was then

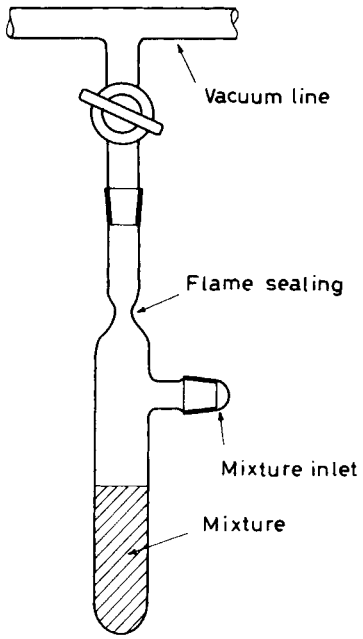

Fig. 1. Device used to prepare the reaction mixtures before irradiation.

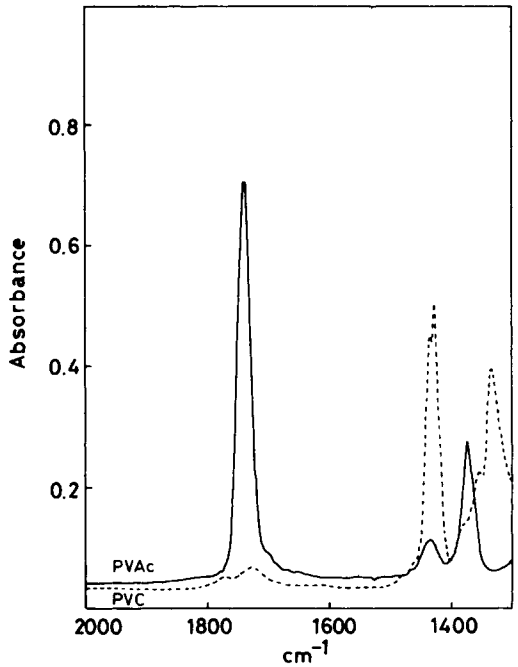

Fig. 2. IR spectra of PVC (---) and PVAc (——).

extracted with boiling methanol (with boiling water in the case of pure PVAc) for at least 12 h.

The polymer was then vacuum dried at 50°C and weighed. In the case of graft copolymers, the ratio PVAc/PVC was evaluated by means of infrared transmission spectroscopy, using a 983 Perkin-Elmer IR spectrometer and a calibration curve prepared with mixtures of PVC and PVAc which had increasing concentration of the latter. The comparison with the experimental samples was performed by evaluating (Fig. 2) the ratio of the 1738 cm^{-1} absorbance peak (typical of =CO vibrations) to the 1433 cm^{-1} one (typical of $=CH_2$). In this way it was possible to measure the amount of PVAc present in the methanol insoluble copolymer.

RESULTS AND DISCUSSION

Vinyl Acetate Homopolymerization

These tests were performed in order to get information on the polymerization of VAc radiochemically induced, in presence of large amounts of DMF. In our opinion, the data obtained are useful to correctly interpret the results of grafting and in particular, the influence of the solvent.

In Figure 3 the percentage of polymer formed is plotted as a function of the irradiation dose, at constant dose rate, in the case of 10% by volume VAc/DMF solutions.

The trend of the above plot shows that the polymerization of VAc in presence of DMF as solvent, somehow follows familiar kinetics.[10] The conver-

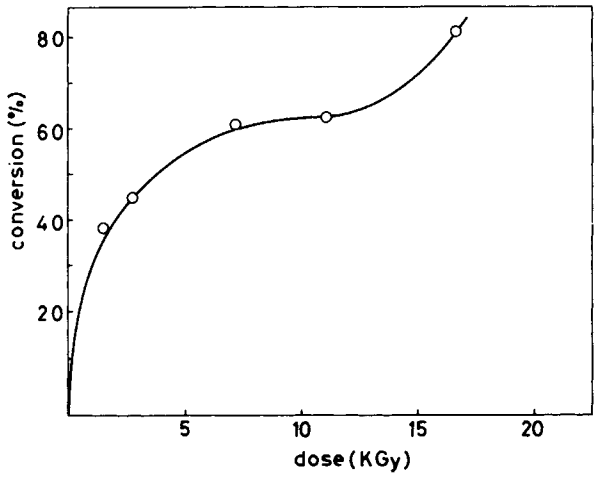

Fig. 3. Conversion plot vs. irradiation dose at 1.92 Gy/min dose rate (10% VAc in DMF mixture).

sion curve is indeed similar to those typical of other monomers as, for instance, acrylates and chloroprene.

As can be seen from Figure 3, after an "induction period" probably due to residual oxygen or radical scavengers (impurities) in the mixture, the polymerization goes on rapidly, thanks to the high radical yield Gr[10] typical of VAc when submitted to gamma irradiation.

When the conversion reaches about 40%, the availability of monomeric molecules decreases, and it results in a lower polymerization rate. Then, at about 60% conversion, the rate increases again with an autoaccelerative trend. This behavior is rather common for radiation induced polymerizations,[10] and it is connected with the apparent decreasing of the termination constant. This phenomenon is controlled by the diffusion and it depends on the viscosity of the system, which increases with the polymer concentration until the so-called "gel effect" hinders the chain termination, enhancing the overall polymerization rate.[10]

As is well known, this behavior has been noticed in many other monomer–solvent systems, when submitted to high energy radiations at constant dose rate, that is, at nearly constant initiation rate, provided that the transfer of the radicals to the solvent is not too high.[15]

In Figure 4 the conversion percent is plotted as a function of the dose rate, keeping constant the radiation dose (2700 Gy). The data show that, as reported elsewhere,[16] the polymerization at constant dose is higher at low dose rates.

This can be explained if we consider that, at low dose rates, to create a certain amount of radicals takes longer than it does at higher rate. Therefore, their instantaneous concentration is generally low and, consequently, the termination probability is also low. This results in a facilitated propagation kinetics, that is higher polymer yield.

The well-known relation

$$R = kI^a \tag{1}$$

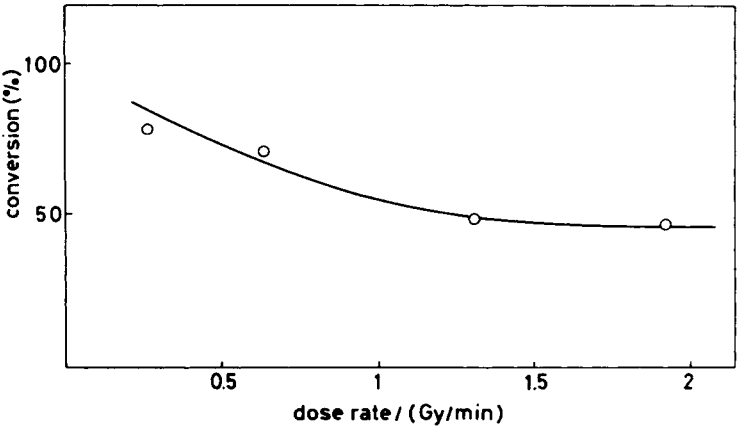

Fig. 4. Percent conversion vs. dose rate at constant irradiation dose (2.7 kGy) and VAc concentration (10%).

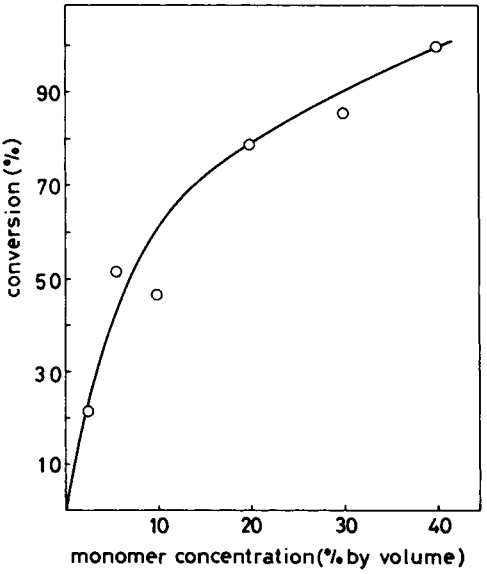

Fig. 5. Influence of the monomer concentration on the polymerization yield at dose rate 1.92 Gy/min and overall dose 2.7 kGy.

which relates polymerization rate R to dose rate I, also suits our case, taking $a = 0.58$, in agreement with the results found elsewhere.[16]

The influence of the concentration of the monomer on the polymerization has also been studied. The tests were carried out at 1.92 Gy/min dose rate and 2700 Gy overall dose.

The plot in Figure 5 shows that the conversion percent increases with monomer concentration and approaches 100 just above 40% of monomer in the original solution. The trend of the plot can be put in relation to some chain transfer mechanisms similar to those already observed elsewhere.[17,18,19]

Grafting of PVC

The gamma radiation causes, in the system PVC/VAc/DMF, both homopolymerization of VAc and its grafting onto the PVC matrix. It is reported that the latter process is facilitated by the high Gr of the PVC.[10]

The so-obtained graft copolymer has some properties of the matrix added to some others typical of PVAc, as could be expected referring to previous similar experiences.[3,4,6,7] Nevertheless, it must be pointed out that, in our case, the grafting goes on in a completely homogeneous phase and the kinetics involved could be somehow different from those reported for heterogeneous or, at least, swollen systems.

The first difference observed concerns the efficiency of separation of the graft copolymer by selective solvents. In our case, the irradiated mixture was water precipitated, then the separation of the homopolymer was done by extraction by boiling methanol, which is reported to be solvent for PVAc and nonsolvent for PVC and PVC-*g*-PVAc. This technique has proven to be unsuitable even at low grafting degrees: the weight changes on the PVC and the infrared analysis have demonstrated that not only PVAc but also PVC can be dissolved in methanol if grafting has taken place to a certain extent.

This could be explained considering the high Gr value for VAc radioinduced polymerization[10] and assuming that the grafting of already developed PVAc chains to PVC is also possible. Such an event can be responsible for the formation of copolymer fractions having chemical characteristics closer than the PVAc's ones. Moreover, working with homogeneous solutions the possibility cannot be excluded for direct "grafting" between two polymers,[2,10] although some experimental tests have demonstrated that in our case this reaction is negligible.

The above-reported phenomenon prevents the evaluation of the grafting yield by usual weight increase measurements. For this reason we used the previously described IR technique, measuring the ratio PVAc/PVC in the

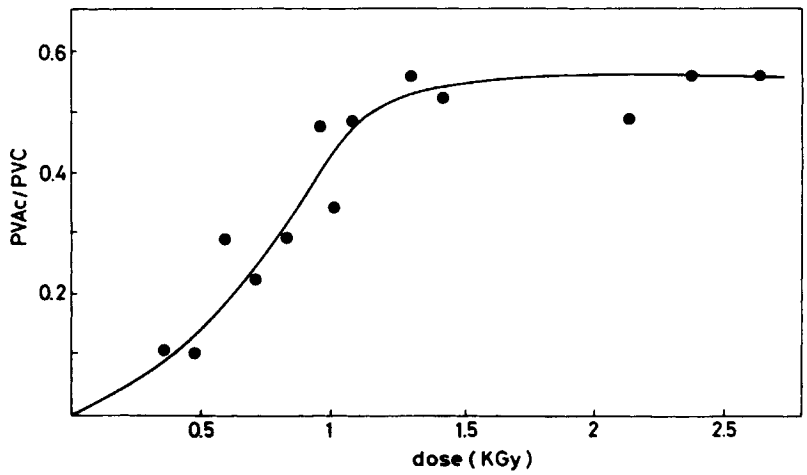

Fig. 6. Ratio of PVAc to PVC in the methanol insoluble fraction of the graft copolymer vs the absorbed dose (dose rate 1.92 Gy/min; initial VAc/PVC ratio: 2.5).

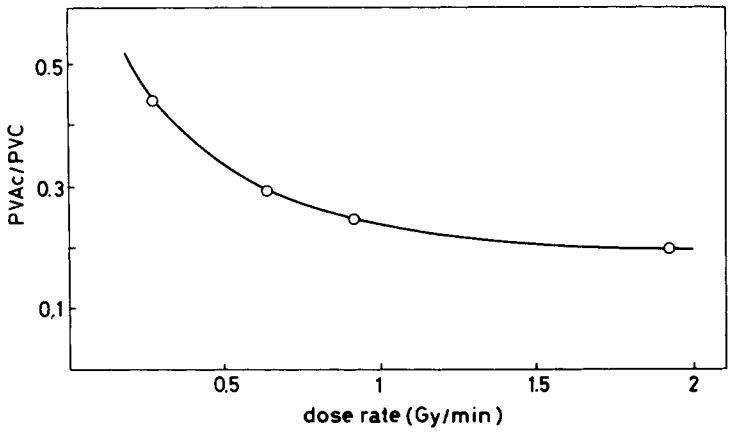

Fig. 7. Influence of the dose rate on the grafting yield at constant dose (0.7 kGy); initial VAc/PVC ratio: 2.5.

methanol insoluble fraction. Such a fraction is the most interesting for applicative purposes.

The plot of Figure 6 shows the ratio PVAc/PVC as a function of the irradiation dose. In this case a solution of 8 g PVC and 20 g VAc in 0.08 dm^3 DMF was irradiated at a dose of 1.92 Gy/min. The interpretation of the plot can be put forward by means of the comments previously reported: I.e., by increasing the absorbed dose, the percentage of grafted chain also increases, and their length as well. Prolonging the radiation time, the graft copolymer begins to show characteristics similar to those of PVAc; the plot thus reaches a maximum value at about 60% ratio. The lack of monomer molecules together with PVAc chains cleavage[20] can also be responsible for the trend at more than 1.5 kGy irradiation doses. Nevertheless, the values of grafted PVAc look fairly high, compared with those obtained during the homopolymerization in the same conditions. This may also be due to the previously mentioned "gel effect": As a consequence of the presence of PVC macromolecules, the viscosity of the system increases.

In this case the length of the grafted chains can also be controlled by the dose rate (Fig. 7) through kinetics described in the case of VAc homopolymerization.

The experimental value of a in relation (1) ranged between 0.48 and 0.56. Nevertheless, it must be pointed out that in these calculations the above-cited "solubilization" phenomenon was not taken into account and thus the numerical values must be considered "apparent" ones.

The ratio PVAc/PVC in the insoluble fraction was also measured as a function of the VAc in original mixture, keeping constant the other conditions (Fig. 8).

Some practical difficulties (crosslinking reaction of the homopolymer, that causes insolubility in methanol) did not allow us to consider the values of PVAc/PVC obtained with more than 60% of monomer in the mixture. Moreover, it can be remarked that the plateau trend of the plot is probably connected with the previously mentioned methanol solubility phenomenon arising when 60% VAc was grafted onto PVC.

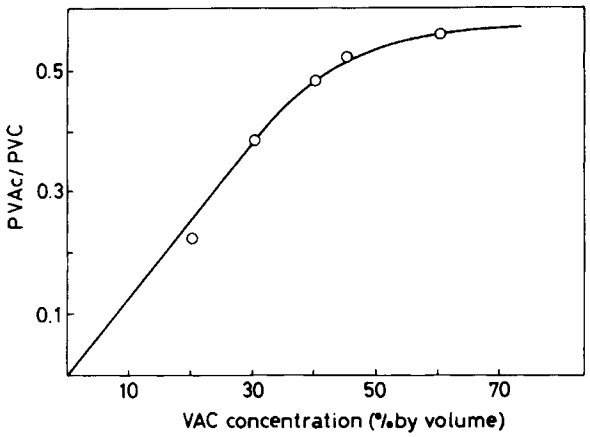

Fig. 8. Influence of the VAc/PVC ratio on the grafting yield. Dose rate: 1.92 Gy/min. Dose: 0.7 kGy.

CONCLUSIONS

The study reported in this paper demonstrates, in our opinion, that it is possible to obtain PVC–VAc graft copolymers starting directly from mixtures of PVC and monomeric VAc dissolved in DMF, by means of gamma irradiation in the absence of oxygen. The grafting reaction seems to be in agreement with kinetics of VAc radioinduced homopolymerization and those found in the case of the grafting of swollen systems. The presence of DMF in large amounts does not interfere with the reaction pathway.

It has, moreover, been ascertained that the graft copolymer consists of two main fractions: one rich in PVC (methanol-insoluble) and the other rich in PVAc (methanol-soluble). The first fraction is suitable for preparation of membranes with the phase inversion technique. Some attempts have already been performed by us, and we hope that we will be able to report the results quite soon.

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