

Radiation Graft Copolymerization of Acrylic Acid and *N*-Isopropylacrylamide from binary mixtures onto Polytetrafluoroethylene

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Summary

Acrylic acid and *N*-isopropylacrylamide were grafted from their binary mixtures in water onto polytetrafluoroethylene films γ -preirradiated in air. Effects of preirradiation dose as well as temperature of grafting on efficiency of this process were investigated, the optimal values of dose and temperature were 20 kGy and 50°C, respectively. The calculated monomers reactivity ratios by their graft copolymerization (r_1 and r_2) were 0.35 and 0.01, respectively. The grafted copolymers exhibited a temperature-responsive character in the range of 17–30°C.

Introduction

At present, there is an essential interest to graft acrylic acid (AAc) and *N*-isopropylacrylamide (NIPAAm) onto polymeric matrices with suitable mechanical properties. These grafted compositions can be employed for biomedical application. The AAc grafted chains act as a reaction sites to introduce various functions through carboxyl groups. Immobilization of bioactive compounds (enzymes, antibodies) onto different polymers preliminary modified via radiation grafting of AAc was studied earlier (1–6). PolyNIPAAm is a water soluble, temperature sensitive polymer which exhibits a lower critical solution temperature (LCST) in the range of 30–35°C (7–10). It has been shown that this polymer can be used for immobilization of proteins, and their activity depended on temperature relatively the LCST (11). Permeability of PE with radiation-grafted polyNIPAAm membranes to riboflavin increased or decreased with temperature depending on grafting yields (12). A drug permeation through a temperature-sensitive polyNIPAAm radiation-grafted onto PVDF membrane was studied (13). Thus, AAc and NIPAAm graft copolymerization onto polymer supports is expected to exhibit new regularities in immobilization and permeability of biocompounds.

Radiation grafting of different monomers (AAc, styrene, acrylonitrile, acrylamide a.o.) from their binary mixtures was performed onto PE, PP, PET and cellulose. (14–19). Kinetics regularities of grafting were determined, and copolymerization reactivity ratios were calculated in some cases. A swelling behavior, electrical conductivity, thermal and mechanical properties were investigated. It seems to be only one work on radiation grafting of two monomers (AAc and 2-hydroxyethyl methacrylate) onto teflon was published (4), but the graft polymerization was not carried out from their binary mixture, the monomers were grafted one after another. Photochemical grafting of AAc and NIPAAm onto PE and cellulose was studied, and temperature-responsive character of the grafted copolymers was analysed (20,21). The grafted copolymers exhibited a temperature-responsive character in the range of 20–40°C.

In the present study, AAc and NIPAAm binary mixtures were grafted onto PTFE γ -preirradiated in air. The monomers reactivity ratios by their graft copolymerization were determined, and a thermoresponsivity of the grafted copolymers was analysed.

Experimental

PTFE films (donated by Laboratoire de Chimie Macromoléculaire sous Rayonnement, CNRS, France) of 85 μm thick and size of 1.5x2 cm were washed in methanol for 24 h, and then dried under reduced pressure to a constant weight.

AAc (Materiales Plasticos S.A. de C.V.) was purified by distillation under a reduced pressure, and NIPAAm (Aldrich Co) purification was carried out by its recrystallization from n-hexane/toluene solution (1/1 in volume ratio).

PTFE samples were irradiated in air at a dose rate of 5.7 kGy/h and radiation doses from 5 to 30 kGy with a ^{60}Co γ -source (Gammabeam 651 PT, Nordion International Inc.). The irradiated films were placed in glass ampoules which contained aqueous solutions of AAc and NIPAAm mixtures with different molar ratios of monomers, and by the constant total monomers concentration of 6M. The ampoules were deaerated by bubbling argon and sealed. Then, they were heated at different temperatures for 15 h. After heating, the samples were washed with water and methanol for 24 h to extract unreacted monomers as well as homopolymers formed during the grafting reaction. The grafted samples were dried under vacuum for 1-2 days to a constant weight.

The grafting yield was calculated by the equation: $\text{Grafting (\%)} = (W - W_0)100/W_0$, where W and W_0 are weights of the grafted and initial films, respectively.

FTIR-ATR spectra of the starting and modified polymers films were analyzed with the Perking-Elmer (model PARAGON) spectrometer. SeZn glass was used for contact with the samples surfaces, and the IR radiation penetrated into samples to depth of 8-10 μm .

Dimensions of the initial and modified samples were measured with micrometer.

Compositions of the grafted AAc-NIPAAm copolymers were determined by elemental analysis in Desert Analytics (Arizona, USA).

Monomers reactivity ratios of AAc (r_1) and NIPAAm (r_2) were calculated by the Fineman-Ross method.

For a measurement of water absorbency, the samples were immersed into phosphate buffer solution (pH=7.0) at different temperatures from 3 to 45 $^{\circ}\text{C}$ up to an equilibrium swelling of the samples was reached. This experiment was carried out in a thermostatic water bath equipped with both heating and cooling systems. The phosphate buffer was used to avoid a swelling responsivity of samples against pH of solution (22). After this procedure, excess of solution on the films surface was wiped by filter paper, and the swelled films were weighted. The samples swelling was calculated as follows: $\text{Swelling (\%)} = (W - W_0)100/W_0$, where W and W_0 are weights of the swelled and initial films, respectively. Thermosensitivity was defined as the ratio of the grafted samples swelling at 3 and 45 $^{\circ}\text{C}$.

Results and discussion

Our preliminary experiments showed a low efficiency of the AAc-NIPAAm grafting by a mutual irradiation of the monomers mixtures with PTFE (direct method) caused by an essential monomers polymerization in their solutions. But grafting onto preirradiated polymers is less complicated with the above-mentioned undesirable process (23), therefore this method of grafting was used. Besides, we found that grafting process is efficient by the chosen dose rate, the total monomers concentration in water of 6M and the grafting time of 15 h.

Figure 1 shows increase in the grafting value with temperature. 50°C can be considered as an optimal temperature which ensure an efficient thermal decomposition of oxidative products, formed by PTFE irradiation in air, to active centers of the grafting initiation.

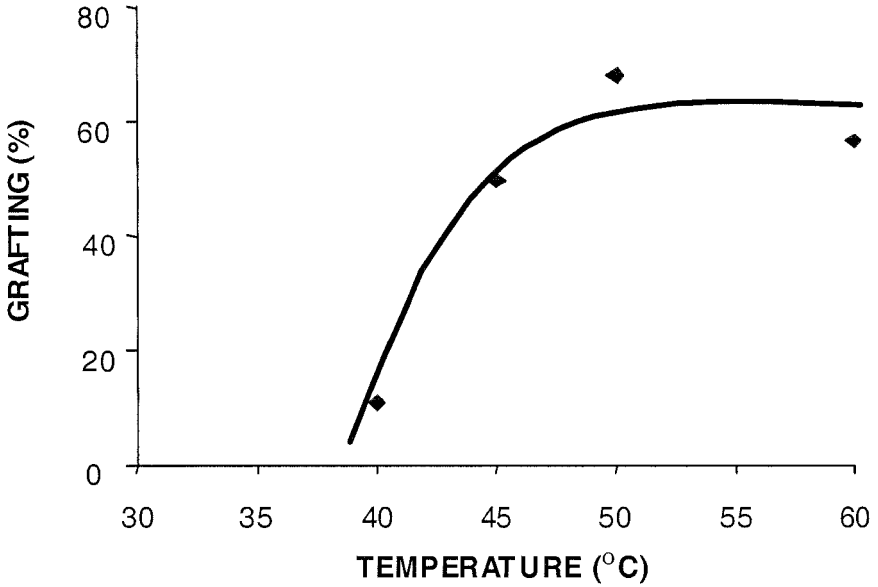


Fig.1. Grafting as a function of temperature. Preirradiation dose 20 kGy, dose rate 5.7 kGy/h, monomers ratio 1/1 M by the total monomers concentration in water of 6M, reaction time 15 h

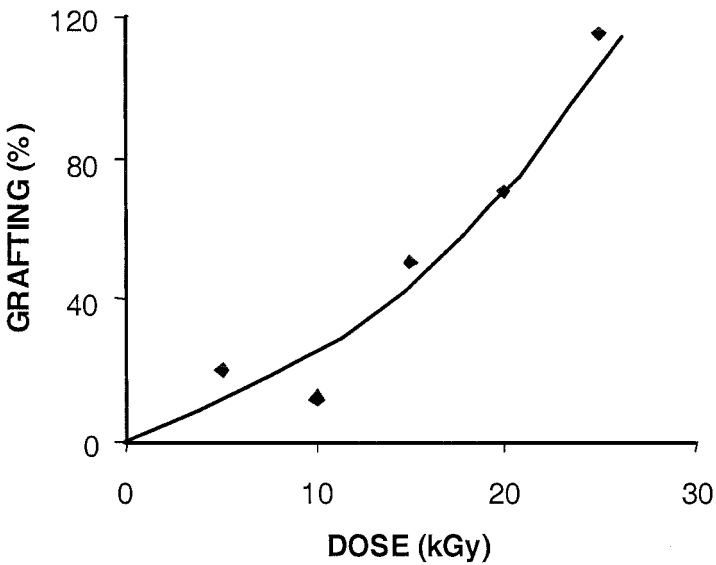


Fig.2. Grafting as function of dose, reaction temperature 50°C, other conditions are the same as in Fig.1

Grafting value increased with dose (Fig.2). It is seen that grafting value is sufficiently high at doses of 15-20 kGy. PTFE is a polymer of low radiation stability, it has a tendency to radiation destruction (24), therefore grafting onto this polymer is performed at relatively low absorbed doses. Thus, preirradiation dose of 20 kGy and grafting temperature of 50°C were used for obtaining of the grafted polymers.

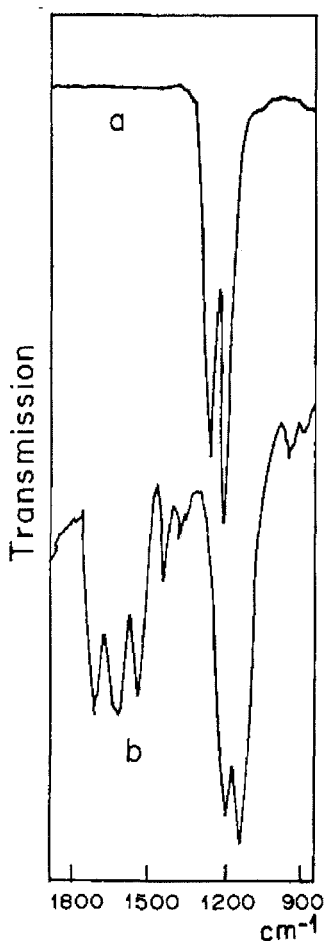


Fig.3. IR spectra of the initial (a) and grafted (b) PTFE

The IR-spectra in a wavenumbers range of 1800-900 cm^{-1} (Fig.3) confirmed the polyAAC and polyNIPAAm grafting onto PTFE. The initial polymer gave two bands at 1203 and 1143 cm^{-1} , the carbonyl groups of AAC are responsible for absorption at 1712 cm^{-1} , and two bands at 1627 and 1552 cm^{-1} are attributed to amide groups of NIPAAm. Monomers reactivity ratios of AAC (r_1) and NIPAAm (r_2) calculated from data of Figure 4 were equal to 0.35 and 0.01, respectively, which indicate that comonomers sequence in the grafted copolymers was highly alternating with some random placement. It should be noted that values of r_1 and r_2 reported by photografting of these monomers from binary mixtures onto PE or cellulose were: 0.95 and 0.38 (20) or

0.89 and 0.47 (21), respectively. This difference between the reported and our data can be explained as follows. It has been found that polyNIPAAm grafted chains localized at the PE surface, while the grafted polyAAc was distributed inside this polymer (20). Therefore, essential parts of AAc did not copolymerize with NIPAAm, and it formed the grafted polyAAc homopolymer that resulted in high value of r_1 . But in our case, the grafted copolymers, probably, were distributed inside the PTFE. It is known that surface grafting is accompanied by a predominant increase in film thickness but the volume grafting is characterized with an approximate uniform increase in thickness and area of the modified samples (25). The latter situation was found for our grafted polymers; for example, increase in the samples thickness and area was of $\sim 30\%$ at 70% of grafting.

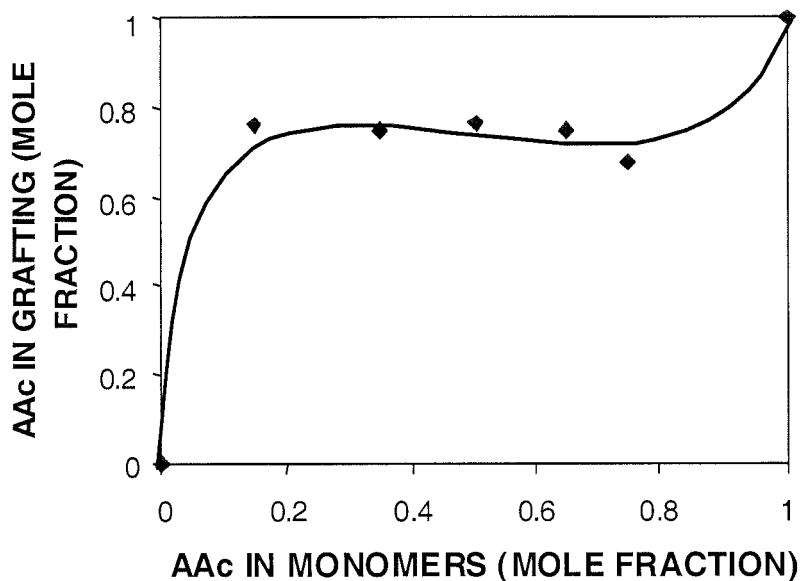


Fig.4. Dependence of grafted copolymers composition on the monomers feed

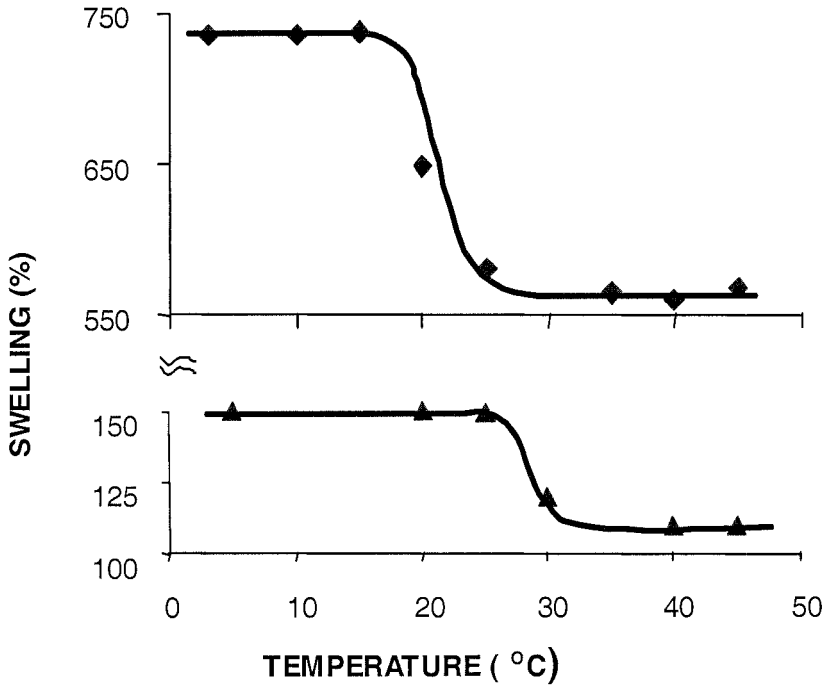


Fig.5. Temperature dependence of equilibrium swelling for the NIPAAm-AAc copolymers grafted onto PTFE. Grafting values (%): 124 (◆) and 65 (▲)

Table 1. Thermosensitivity and LCST for the grafted samples

Grafting (%)	Thermosensitivity	LCST (°C)
124	1.3	20
65	1.4	27

Fig.5 shows the samples swelling at different temperatures. It is seen that swelling steeply decreased with increasing in temperature. The grafted copolymers exhibited a temperature-responsive character in the range of 17-30°C which is close to data obtained by graft copolymerization of these monomers onto PE (20). But insignificant difference in the thermosensitivity and LCST values as a function of the grafting percent (Table 1) can be explained by the same ratio of the AAc and NIPAAm components in the grafted copolymer, according to data in Fig.4.

Conclusion

The efficient grafting of AAc and NIPAAm from their binary mixtures in water was performed onto PTFE γ -preirradiated in air. The optimal values of the preirradiation dose and grafting temperature were 20 kGy and 50°C, respectively. The calculated monomers reactivity ratios by their graft copolymerization (r_1 and r_2) were 0.35 and 0.01, respectively. The grafted copolymers exhibited a temperature-responsive character in the range of 17-30°C. Their thermosensitivity and LCST practically did not depend on the grafting values.

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