Radiation grafting of N,N-dimethylaminoethylmethacrylate and 4-vinylpyridine onto polypropylene by the one- and two-step methods

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Summary

Radiation grafting of N,N-dimethylaminoethylmethacrylate (DMAEMA) and 4-vinylpyridine (4-VP) from the 50% monomers solutions in toluene and dichloroethane onto polypropylene (PP) films was carried by their mutual γ-irradiation (one-step method). In the two-step method, the grafting of DMAEMA or 4-VP from their solutions in toluene was performed onto PP modified preliminary with the other polymer (poly4-VP or polyDMAEMA). It has been found that chemical structure of PP modified with the first grafted polymer affected the efficiency of the other monomer grafting by the second step.

Introduction

In recent years there has been increasing interest in developing novel functional materials based on the use of strong noncovalent interactions for holding together molecular components (1-3). The system consists in mixing one functional homopolymer and one functional compound. The main application of this concept is the design of polymeric liquid crystalline (LC) materials. It is known that homopolymers obtained from monomers, containing tertiary amino groups, such as N,N-dimethylaminoethyl-methacrylate (DMAEMA) or 4-vinylpyridine (4-VP) form salts with several benzoic acid derivatives but these compounds are often hygroscopic and have poor mechanical properties (2,3). Therefore preliminary graft polymerization of these monomers onto hydrophobic and mechanically durable polymer matrices is of interest. Radiation grafting of DMAEMA onto polyethylene (PE) as well as salts of poly(DMAEMA-g-PE) with benzoic acids formation were reported earlier (4,5).

Choice of matrices is conditioned also by their transparency and melting points that should be higher than mesophase temperature of the grafted polymeric salts. Isotactic polypropylene (PP) is a transparent and durable polymer with melting point about of 170^0C, and it can be considered as a promising material for monomers grafting with following immobilization of LC.

Radiation grafting of DMAEMA or 4-VP onto PP has been reported earlier (6-12) but practically only the polymer preirradiation method was used. Direct method of grafting, when a polymer is irradiated in close contact with a monomer, is more effective, as compared with the preirradiation method, and it enables, as a rule, a more fine regulation of the grafting value with the absorbed dose (13). Grafting of these monomers onto polymers by the two-step method has never been investigated before but there are data on

polymers modification by this method using other monomers: acrylic acid, acrylamide and N-isopropylacrylamide (14,15).

This work presents the results of a study on modification of PP by direct grafting of DMAEMA or 4-VP to the starting polymer (one-step method), and additional grafting each of these monomers to the PP modified preliminary with the other polymer (two-step method).

Experimental

Films of isotactic PP (PEMEX, Mexico) with a thickness of 70 μm were cut into 1x5 cm pieces. DMAEMA and 4-VP (Aldrich Chemical Co) was purified by distillation under a reduced pressure.

For the PP swelling to be characterized, samples were immersed in pure DMAEMA or 4-VP as well as in 50 vol% solutions of these monomers in toluene, dichloroethane (DCE) or methanol at room temperature until equilibrium swelling was reached. Then samples were taken out and the excess solution deposited on the film surface was removed quickly with blotting paper, and samples were weighed. The swelling degree was calculated by the equation:

$$\text{swelling } (\%) = (W - W_o)100/W_o$$

where W and W_o are the weights of swollen and dry samples, respectively.

PP films were placed in glass ampoules which contained pure DMAEMA, 4-VP, or their 50% solutions in toluene or DCE. The reaction mixtures were deaerated under vacuum by repeated freezing and thawing method, ampoules were sealed and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at a dose rates of 0.45 or 5.5 kGy/h and doses from 1 to 40 kGy. To extract the residual monomers and homopolymer that could be formed and occluded in the films during the irradiation, the samples grafted with polyDMAEMA were washed with toluene for 10 h, but samples grafted with poly4-VP were washed with dimethylformamide and methanol. Then samples were dried under vacuum to a constant weight. The grafting yield was calculated by the same equation as for a swelling degree, where W and W_0 are the weights of the grafted and starting samples, respectively.

Swelling of PP with the grafted poly4-VP in DMAEMA solution or PP with the grafted polyDMAEMA in 4-VP solution (50% solutions of monomers in toluene were used in both cases) was carried out by the aforesaid technique. Then graft polymerization of DMAEMA or 4-VP from these solutions was performed onto PP modified preliminary with the other polymer. The same extraction and drying procedures were used as by the grafting onto the starting PP. But in this part of the work, the swelling and grafting values were calculated against W_0 as a weight of the preliminary modified sample.

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

Results and discussion

Swelling of polymer in monomer solution is effective in radiation graft polymerization due to closeness of monomer molecules inside the swollen polymer matrix to the active centers of a grafting initiation which are formed in the irradiated polymer (13). Besides, a

use of pure monomers in a graft polymerization is restricted by their undesirable homopolymerization initiated by the polymer-monomer systems irradiation in the direct method. Contribution of homopolymerization is less or negligible with decrease in monomer concentration. PP practically did not swell in pure DMAEMA, 4-VP and in their methanol solutions but swelled a little (8-10%) in solutions of the monomers in DCE and toluene. These solvents have been chosen for the grafting experiments.

It is known that PP is a radiation-crosslinkable polymer but essential changes in its structure, caused by γ-irradiation, occur at doses of about 100 kGy and more (16). The relatively low doses of irradiation, used in the present work, did not change the irradiated PP swelling in monomers solutions as compared with the starting polymer.

Fig.1 shows higher rates of the DMAEMA and 4-VP grafting at the dose rate of 5.5 kGy/h as compared with 0.45 kG/h. Besides, grafting at 0.45 kGy/h was complicated with essential homopolymerization of the monomers used. Therefore 5.5 kGy/h can be considered as a more appropriate dose rate for these monomers grafting onto PP.

It is seen from Fig.2 that efficiency of graft polymerization depended essentially on the presence of solvents in the monomers mixtures. In the case of grafting from pure 4-VP, a strong monomer homopolymerization was observed, and yield of grafting was relatively low. An attempt to graft DMAEMA from the pure monomer was unsuccessful, and only polyDMAEMA homopolymer was formed by the polymer-monomer irradiation. It should be noted that grafting of DMAEMA and 4-VP from their solutions in toluene and DCE was characterized with a different efficiency but this process was not accompanied by an essential monomers homopolymerization especially in the presence of toluene.

Equilibrium swelling of the modified PP in 50% monomers solutions in toluene was higher in contrast to the starting PP, and increased with the poly4-VP or polyDMAEMA content (grafting percent) in PP. The swelling values reached ~100% for the PP with grafted poly4-VP (95%) immersed in DMAEMA solution, and ~150% for the PP with grafted polyDMAEMA (105%) immersed in 4-VP solution.

In spite of the essential swelling of PP, modified with the first polymer (poly4-VP or polyDMAEMA), in solutions contained the second monomer (DMAEMA or 4-VP), the efficiency of these monomers grafting decreased with an increase in content of the first grafted polymer in PP (Figs 3 and 4). This fact may be explained by the difference in radiation-chemical yields (G) of radicals that are responsible for the grafting initiation, and which are formed in PP, poly-4-VP and polyDMAEMA by their direct irradiation. The G values in irradiated PP are within 0.5-1.2 radicals/100 eV (17), and it seems to be no G data for the irradiated poly-4-VP and polyDMAEMA. But it is known that G values are significantly less for polymers contained aromatic groups as compared with the aliphatic ones, and G are equal to 0.08 and 0.02 for the irradiated polystyrene and poly(ethylene terephthalate), respectively (17). Thus, the less efficient grafting of DMAEMA onto PP-poly4-VP composition as compared with the grafting onto the starting PP (Fig.3) may be explained by influence of the aromatic 4-VP groups in this composition. Probably, the analogous effect was responsible for the grafting decrease in the case of 4-VP graft polymerization onto PP-polyDMAEMA composition (Fig.4).

The IR-spectra analysis of the starting and modified PP in a wavenumbers range of 1800-1300 cm^{-1} (Fig.5) confirmed the polyDMAEMA and poly4-VP grafting onto PP; the spectra of samples, contained both modifying polymers, were identical qualitatively (d) independent on a sequence of the monomers grafting. The methyl groups of PP gave
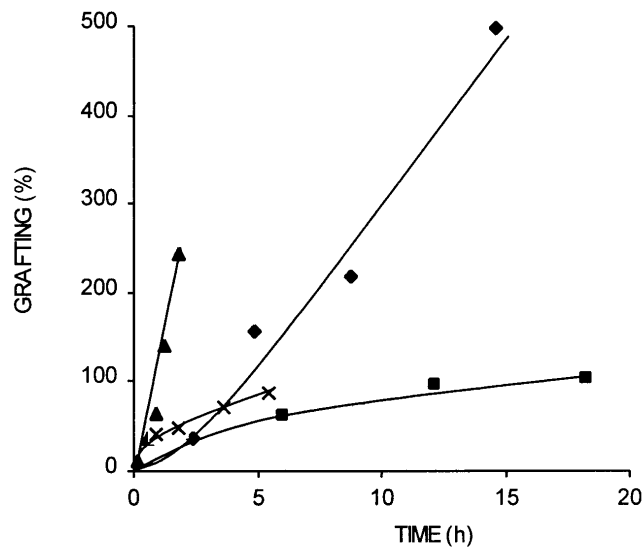
Fig.1. Grafting of DMAEMA and 4-VP in DCE as a function of irradiation time.
DMAEMA: 5.5 kGy/h (×), 0.45 kGy/h (■); 4-VP: 5.5 kGy/h (▲), 0.45 kGy/h (♦)
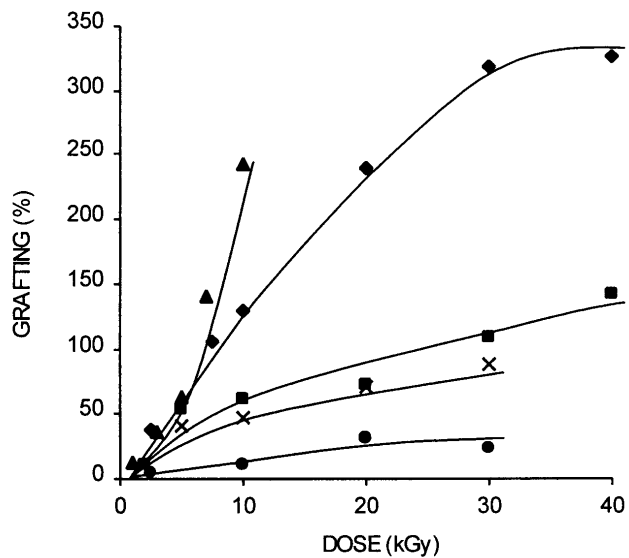

Fig.2. Grafting of DMAEMA and 4-VP as a function of dose. Dose rate 5.5 kGy/h.
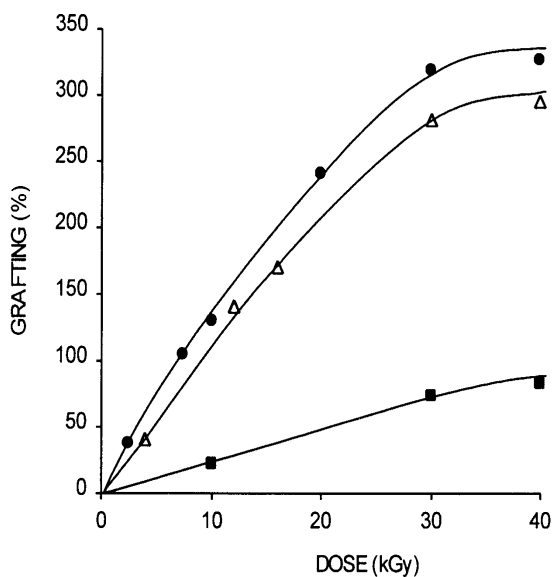DMAEMA: in DCE (×), in toluene (♦); 4-VP: pure (●), in DCE (▲),
in toluene (■).

Fig.3. Grafting of DMAEMA from 50% toluene solution onto PP (●)
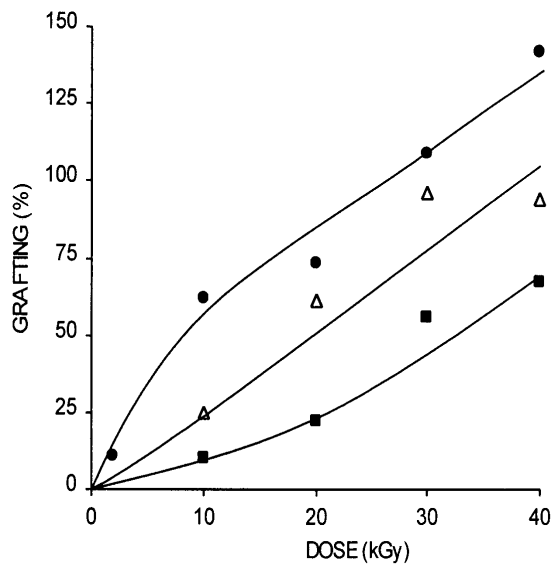and PP with grafted poly4-VP: 25% (Δ) and 95% (■)

Fig.4. Grafting of 4-VP from 50% toluene solution onto PP (●)
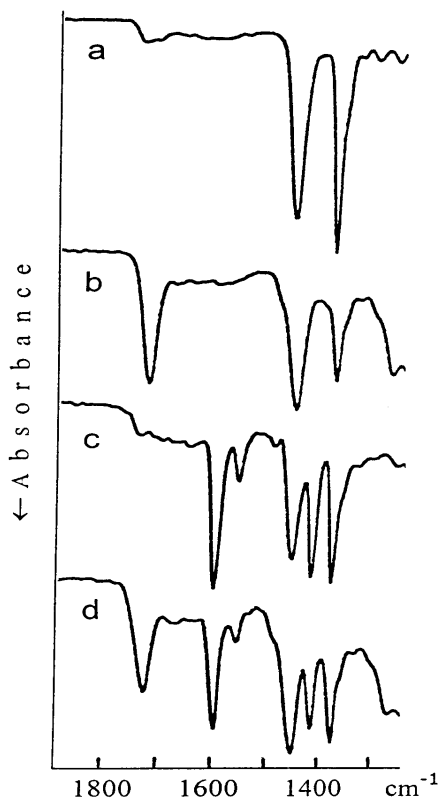and PP with grafted polyDMAEMA: 38% (Δ) and 105% (■)

Fig.5. IR spectra of the starting and modified PP: (a) PP, (b) PP with polyDMAEMA (63%), (c) PP with poly4-VP (64%), (d) PP with polyDMAEMA and poly4-VP (132% total).

two vibration bands at 1454 and 1374 cm^{-1} (all spectra), the carbonyl group of DMAEMA is responsible for a strong absorption at 1724 cm^{-1} (b and d), and three peaks at 1595, 1555 and 1414 cm^{-1} (c and d) can be attributed to the pyridine ring stretching vibration (18).

The grafting process affected the films thickness, and, for example, at ~100% of the DMAEMA or 4-VP grafting this thickness increased for ~50% but areas of the samples did not practically change. The same tendencies were observed by the two-step method. It is known that location of the grafted chains predominantly near surface of the modified polymeric films is accompanied by the increase in their thickness without essential changes in the area (19). It is possible to assume that in our case the grafted polyDMAEMA and poly4-VP are distributed in PP films non-uniformly and they are located mainly near this polymer surface.

Conclusion

Mutual γ-irradiation of PP and solutions of DMAEMA or 4-VP in toluene or DCE resulted in the effective grafting onto PP. It has been found that chemical structure of PP modified with the first grafted polymer affected the grafting efficiency by the second step. Different dependence of thickness and area of the modified films on the grafting value testify to predominant location of the grafted chains near the PP surface.

Acknowledgements

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