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Graft polymerization of *N,N*-dimethylaminoethylmethacrylate onto polycarbonates by the preirradiation method

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Summary

Radiation-induced graft polymerization of N,N-dimethylaminoethylmethacrylate (DMAEMA) from solutions in carbon tetrachloride or in chloroform onto bisphenol A-derived polycarbonate (PC-1) and allyl diglycol carbonate (PC-2), respectively, was carried out by method of preirradiation in air. It has been found essential difference in transparency and durability of the modified PC-1 and PC-2. Effects of preirradiation dose as well as temperature and time of graft polymerization on effectiveness of DMAEMA grafting onto PC-2 were investigated, the optimal values of dose and temperature are 500 kGy and 55°C, respectively.

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 dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide and dimethylaminopropylacrylamide 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 the above-mentioned monomers onto hydrophobic and mechanically durable polymer matrices is of interest. Radiation grafting of DMAEMA onto PE and PP has been investigated 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. Polycarbonates are transparent and durable polymers, some of them have relatively high melting points and can be considered as promising materials for monomers grafting with following immobilization of LC. It is known that bisphenol A-derived polycarbonate melts above 200°C (6), our preliminary testing of di(ethylen glycol) bis allyl dicarbonate with DSC method showed that this polymer did not melt up to 250°C. Effects of the ionizing radiation on properties of polycarbonates, mainly based on bisphenol A-derived one, has been investigated by many authors (7-15). It has been shown that polycarbonates irradiation results in its scission but mechanical properties hardly change up to a dose of 1000 kGy.

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Grafting of monomers onto polymers preliminary irradiated in the presence of air (peroxide method) is widely used for polymers modification (16).

This work presents the results of a study on graft polymerization of DMAEMA onto bisphenol A-derived polycarbonate (PC-1) and di(ethylen glycol) bis allyl dicarbonate (PC-2) γ-preirradiated in air.

Experimental

Plates of PC-1 (Goodfellow Cambridge Ltd., England) and PC-2 (Page Ltd, England) with a thickness of 250 µm were cut into 1x5 cm pieces. DMAEMA (Aldrich Chemical Co) was purified by distillation at a reduced pressure. For the swelling to be characterized, the PC-1 and PC-2 plates were immersed in 50 vol % solution of DMAEMA in carbon tetrachloride or in chloroform 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:

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

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

Polycarbonates plates were irradiated in air with a ^{60}CO γ-source (Gammabeam 651 PT, Nordion International Inc.) at a dose rate of 7.8 kGy/h and at room temperature. The irradiated samples were placed in glass ampoules which contained 50 vol % solution of DMAEMA in carbon tetrachloride (PC-1) or in chloroform (PC-2). The ampoules were deaerated by repeated freezing and thawing method, sealed under vacuum, and then placed in water bath at temperatures from 30 to 65°C for 1 to 12 h. After heating, the unreacted monomer and polyDMAEMA homopolymer formed were extracted from samples with chloroform or with carbon tetrachloride for 24 h, and samples were dried under vacuum for 1-2 days to a constant weight. The grafting yield was determined gravimetrically as weight percent.

Results and discussion

Irradiation of PC-1 and PC-2 plates in air up to 1000 kGy did not lead to increased fragility but samples became yellowish without loss in transparency.

PC-1 and PC-2 swelling in DMAEMA solution.

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 grafting initiation which are formed by thermal decomposition of peroxides and hydroperoxides in polymer preirradiated in air. Besides, pure monomer using in graft polymerization via preirradiation method is restricted by undesirable homopolymerization of monomer initiated with the OH radicals (products of the hydroperoxydes decomposition), contribution of this process is less or negligible with decrease of momomer concentration.

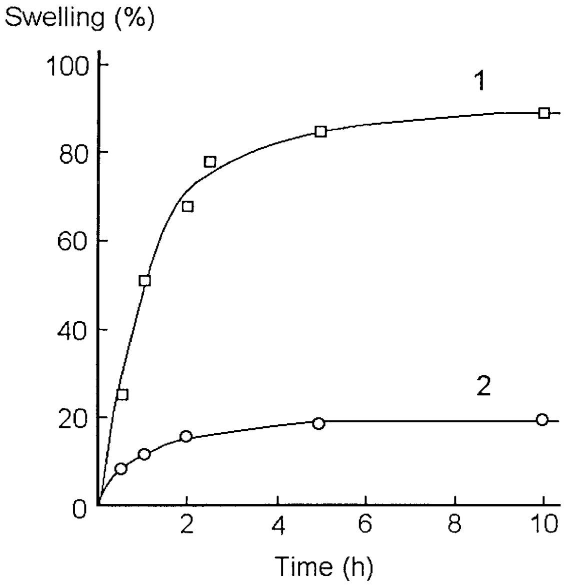

Fig.1. Swelling of PC-1 (1) and PC-2 (2) in 50% solutions of DMAEMA in carbon tetrachloride or chloroform, respectively.

PC-1 well swelled in DMAEMA solution in carbon tetrachloride (Fig.1) but swelling resulted in partial loss of polymer transparency. It should be noted that contact of PC-1 with monomer solutions, contained other swelling agents for this polymer (chloroform and acetone), leads to the same deterioration of PC-1 transparency. PC-2 did not swell in DMAEMA solution in carbon tetrachloride but slowly swelled in solution of this monomer in chloroform without visual changes in its transparency.

DMAEMA grafting onto PC-1.

Grafting from solution in carbon tetrachloride resulted in essential deterioration of the samples transparency, and they became fragile. PolyDMAEMA content reached 13-14% for samples preirradiated at dose of 150 kGy and grafted at 30°C for 12 h. Changes in monomer concentration or in temperature of grafting led to the same unsatisfactory optical and mechanical properties of the modified PC-1 that makes its application dufficult for obtaining compositions with LC immobilized of good quality.

DMAEMA grafting onto PC-2.

This monomer grafting from solution in chloroform did not result in changes of samples transparency and durability.

Effect of grafting temperature was investigated. Grafting depended essentially on temperature and reached maximal value at 55°C (Fig.2) that was explained by effective thermal decomposition of peroxides and hydroperoxides in irradiated PC-2 at this temperature. It has been shown earlier that optimal temperature of DMAEMA grafting by this method may be different and it depended on nature of polymer used (4,5).

Effectiveness of grafting depends essentially on dose of preirradiation. Fig.3 shows that it is necessary to irradiate PC-2 in air up to 500 kGy for maximal value of grafting. It is a relatively high dose of preirradiation by comparison with other polymers (PE and PP) used for DMAEMA grafting (4,5). This difference may be explained by less radiation-chemical yield of radicals in PC-2 during irradiation that resulted in lower concentration of peroxides and hydroperoxides in it, after radicals interaction with oxygen of air.

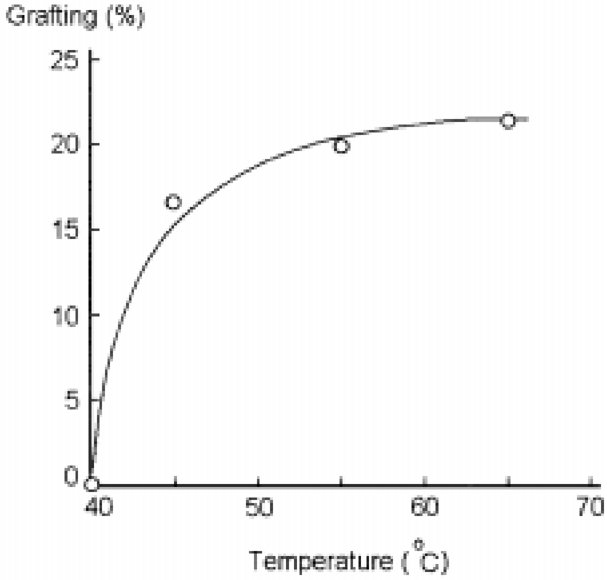

Fig.2. Grafting onto PC-2 as a function of temperature. Dose 500 kGy, reaction time 2 h.

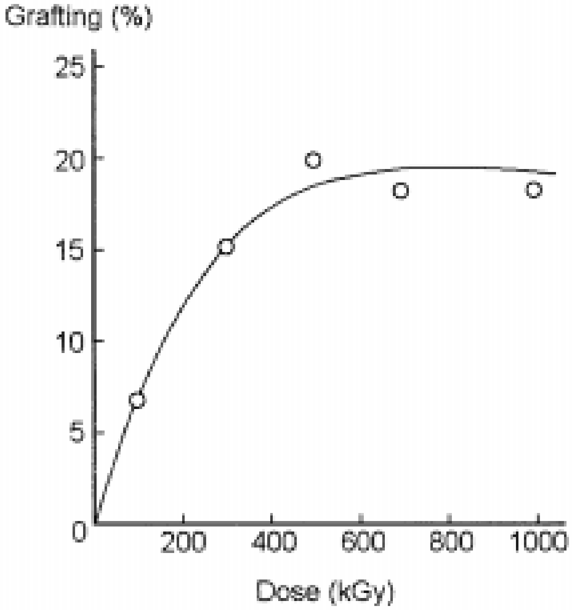

Fig.3. Grafting onto PC-2 as a function of dose. Temperature 55°C, reaction time 2 h.

Fig.4 shows kinetics of DMAEMA grafting onto PC-2 under optimal preirradiation dose and grafting temperature.

It has been shown earlier that peroxides and hydroperoxides formed in polymers, preirradiated in air, are stable at room temperature that gives possibility to keep irradiated polymer for a long time before performing a grafting process (17). For example, peroxides in irradiated cellulose were stable to initiate graft polymerization several years after their formation. In our case, storage of PC-2, irradiated in air, did not affect on grafting value (Fig.5) that indicate to stability of peroxides and hydroperoxides in this polymer at ambient temperature.

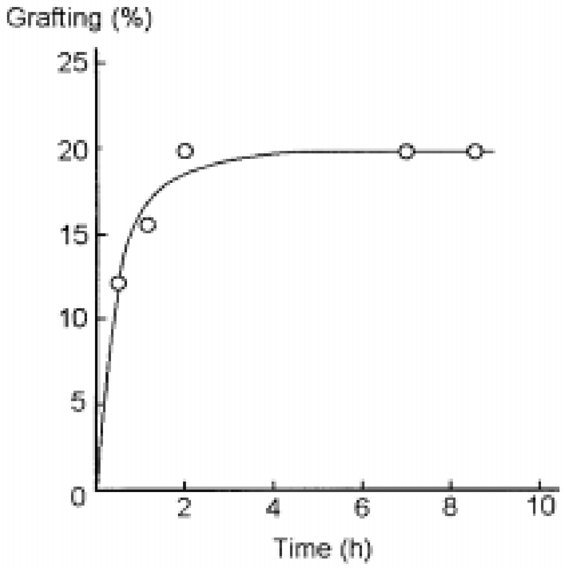

Fig.4. Grafting onto PC-2 as a function of reaction time.
Dose 500 kGy, temperature 55°C.

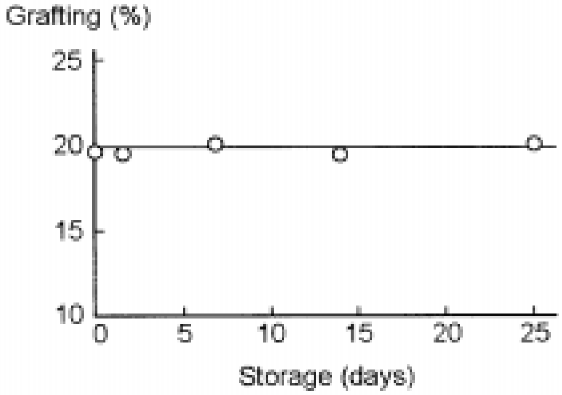

Fig.5. Effect of preirradiated PC-2 storage on grafting. Dose 500 kGy, temperature and time of grafting are 55°C and 2 h.

Conclusion

Graft polymerization of DMAEMA from solutions in carbon tetrachloride or in chloroform onto PC-1 and PC-2, preirradiated in air, resulted in their different properties. Modified PC-2 had transparency and durability that practically did not change from the starting polymer. Optimal dose of preirradiation, temperature and time of graft polymerization were found for DMAEMA grafting onto PC-2: 500 kGy, 55°C and 2 h. But modification of PC-1 led to essential deterioration of the samples transparency and their fragility, grafting of DMAEMA onto PC-1 under given conditions can not be recommended for obtaining of compositions of good quality.

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