Polymer Bulletin 44, 331–335 (2000)

Polymer Bulletin

Radiation grafting of *N,N*-dimethylaminoethylmethacrylate onto poly(ethylene terephthalate)

M. P. Carreón[1], R. Aliev[2,*], R. Ocampo[2], G. Burillo[2]

[1] Institut de Physique et Chimie des Matériaux de Strasbourg, 23 Rue du Loess,
67037 Strasbourg Cedex, France
Permanent address: Instituto de Ciencias Nucleares, UNAM, Ciudad Universitaria,
04510, Mexico D.F., Mexico
[2] Instituto de Ciencias Nucleares, UNAM, Ciudad Universitaria, 04510, Mexico, D.F., Mexico

Received: 18 November 1999/Revised version: 7 February 2000/Accepted: 8 February 2000

Summary

Radiation-induced graft polymerization of N,N-dimethylaminoethylmethacrylate (DMAEMA) from 50% solution in chloroform onto poly(ethylene terephthalate) (PET) was carried out by means of mutual γ-irradiation of polymer in presence of liquid or vapor phase monomer solutions (direct method), or by grafting of monomer from this liquid solution onto polymer preirradiated in air. It has been shown higher effectiveness of grafting by the direct method from vapor phase of monomer or by the preirradiation method as compared with direct grafting from liquid monomer solution. Grafting did not affect crystallinity, transparency and durability of the starting PET.

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. Poly(ethylene terephthalate) (PET) is a transparent and durable polymers with melting point above 250°C, and it can be considered as a promising material for monomers grafting with following immobilization of LC.

For irradiated PET both crosslinking and degradation are possible but some damage in this polymer, caused by irradiation, were observed at doses of 10^3 kGy and more (6). Radiation grafting of different monomers (acrylic acid, acrylonitrile, styrene a.o.) onto PET has been investigated earlier, grafting was carried out by direct or preirradiation methods from the monomers liquid phase (7-11). It should be noted that number of

---

[*] Corresponding author

publications on PET modification via radiation grafting is essentially less as compared with other widespread polymers (polyolefins, PVC etc).

This work presents the results of a study on graft polymerization of DMAEMA onto PET by means of mutual irradiation of polymer in presence of liquid or vaporous monomer solutions in chloroform (direct method), or by grafting of monomer from this liquid solution onto polymer preirradiated in air.

Experimental

Plates of PET (Goodfellow Cambridge 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, samples were immersed in pure DMAEMA or in 50 vol % solution of DMAEMA 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:

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

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

For direct grafting from liquid phase of monomer, polymer samples and 50% monomer solutions in chloroform were placed in glass ampoules. But for vapor phase grafting, samples were placed above this liquid solution in ampoules of special construction to ensure contact of polymer with the monomer-solvent vapor. In both cases, the ampoules were deaerated by repeated freezing and thawing method, sealed under vacuum, kept for 5-6 h, and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at a dose rate of 4 kGy/h. For vapor phase grafting, a lower part of ampoules, contained liquid monomer solution, was protected with a lead against irradiation to reduce DMAEMA homopolymerization. For grafting by the preirradiation method, the PET plates were irradiated in air at a dose rate of 11 kGy/h. The irradiated samples were placed in glass ampoules which contained monomer solution in chloroform. The ampoules were sealed under vacuum, and then placed in water bath at temperatures from 40 to 65°C for 1 to 10 h.

After all these procedures, the unreacted monomer and polyDMAEMA homopolymer formed were extracted from samples with chloroform 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 of grafted polyDMAEMA in the modified PET.

Crystallinity of samples was analyzed using a Siemens D-500 diffractometer with Cu K_α radiation of 1.5406 Å wavelength.

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 grafting initiation which are formed in polymer irradiated in absence of oxygen or by thermal decomposition of peroxides and hydroperoxides in polymer preirradiated in air. Besides, pure monomer using in graft polymerization is restricted by undesirable homopolymerization of monomer initiated both by its direct irradiation and with the OH

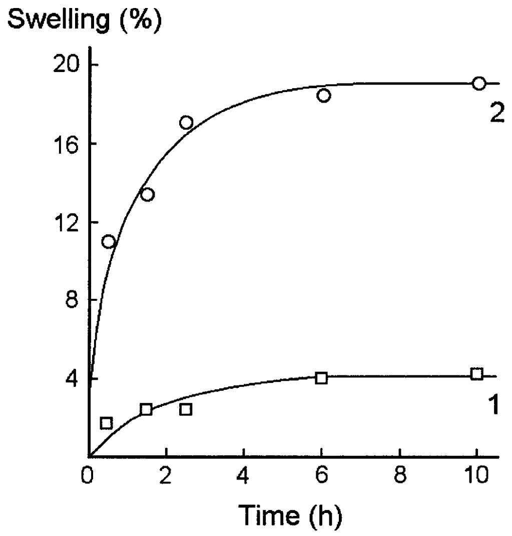

Fig.1. PET swelling in DMAEMA (1) and in 50% monomer solution in chloroform (2).

radicals (products of the hydroperoxydes decomposition). Contribution of homopolymerization is less or negligible with decrease of monomer concentration.

Fig.1 shows essential difference in the PET equilibrium swelling in pure DMAEMA and in monomer solution in chloroform.

Low effectiveness of DMAEMA grafting from liquid monomer solution by the direct method (Fig.2) is explained by strong monomer homopolymerization at the doses used; at doses of 10-20 kGy monomer solution became viscous. But direct grafting from vapour phase led to essential increase in grafted polyDMAEMA content. This fact may be explained by lower monomer concentration in vapor due to essential difference in volatility of DMAEMA and chloroform with following relatively lower monomer

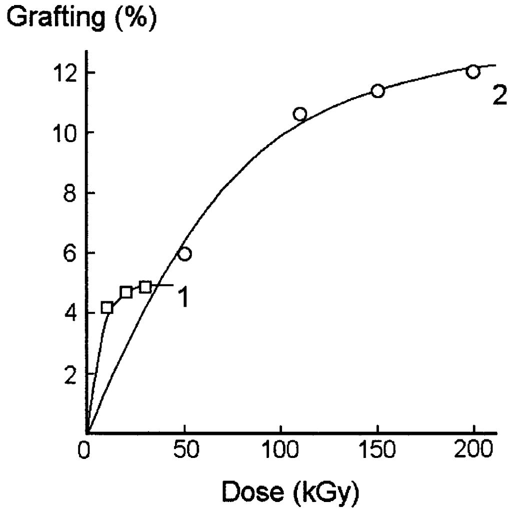

Fig.2. Direct grafting of DMAEMA onto PET from liquid (1) and vapor (2) phase of 50% monomer solution in chloroform. Dose rate 4 kGy/h.

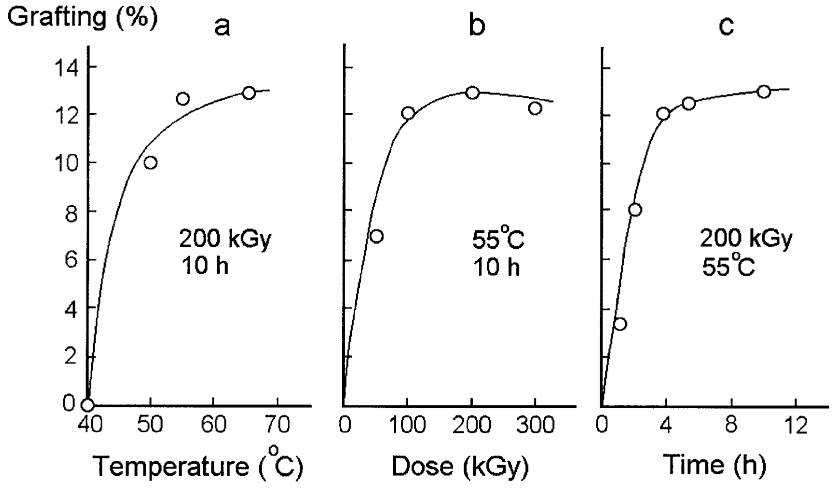

Fig 3. Grafting of DMAEMA onto PET by the preirradiation in air method as a function of different parameters. Dose rate 11 kGy/h.

concentration sorbed in polymer as compared with the initial liquid monomer-solvent mixture. Monomer homopolymerization is essentially less under this condition (12). Effect of monomer concentration on grafting rate is confirmed by different slope of curves 1 and 2 at the initial stage of this process.

For the preirradiation in air method, effect of grafting temperature was investigated. Grafting depended essentially on temperature and reached maximal value at 55°C (Fig.3a) that was explained by effective thermal decomposition of peroxides and hydroperoxides in the irradiated PET at this temperature. Effectiveness of grafting depends essentially on dose of preirradiation, it is necessary to irradiate PET in air up to 200 kGy for maximal value of grafting (Fig.3b). Fig.3c shows kinetics of DMAEMA grafting onto PET under optimal preirradiation dose and grafting temperature. These results indicate to optimal dose of PET preirradiation, temperature and time of DMAEMA grafting: 200 kGy, 55°C and 10 h. Grafting by this method practically was not accompanied by monomer homopolymerization, viscosity of monomer solution did not change.

Relatively low values of DMAEMA grafting onto PET in comparison with other polymers (4,5) may be explained by low radiation-chemical yield of radicals in PET (9). Crystallinity of the modified PET did not change from the starting one, and was equal to 79-80%. It has been shown earlier (13) that grafting up to 20% mainly took place in amorphous layers without distortions in crystalline phase of polymer. But increase in concentration of grafted chains was accompanied by decrease of polymer crystallinity (5). DMAEMA grafting did not affect practically on transparency and durability of the PET.

Conclusion

Effective radiation graft polymerization of DMAEMA from 50% solution in chloroform onto PET was accomplished by the direct method from vapor phase of monomer solution or by the preirradiation in air method from liquid phase of this solution, and grafting values reached 12-13% in these cases. Effectiveness of grafting by the direct method from liquid phase of monomer was low because of strong monomer homopolymerization. Modified PET had crystallinity, transparency and durability that practically did not change from the starting polymer.

Acknowledgements

The authors are indebted to S.Ham and F.García from ICN-UNAM for their technical assistance, and to CONACyT for the financial support (project I 27988-U).

References

1. Ujiie S, Iimura K (1992) Macromolecules 25:3174
2. Bazuin CG, Brandys FA, Eve TM, Plante M (1994) Makromol Chem Macromol Symp 84:183
3. Bazuin CG, Tork A (1995) Macromolecules 28:8877
4. Bucio E, Burillo G (1997) Polym Bull 38:587
5. Bucio E, Aliev R, Burillo G (1998) Radiat Phys Chem 52:193
6. Ivanov VS (1992) Radiation Chemistry of Polymers. VSP. Utrecht. pp 124,198
7. Kale PD, Lokhande HT, Rao KN, Rao MH (1975) J Appl Polym Sci 19:461
8. Sundardi F (1979) Polymer 20:1522
9. Rao MH, Rao KN (1985) Radiat Phys Chem 26:669
10. Hsieh Y-L, Shinawatra M, Castillo MD (1986) J Appl Polym Sci 31:509
11. Zhitariuk NI, Shtanko NI (1990) Eur Polym J 26:847
12. Tsetlin BL, Babkin IYu, Kabanov VYa, Ponomarev AN (1985) High Energy Chem 19:244
13. Cackovic H, Loboda-Cackovic J, Hoseman R (1973) J Polym Sci Polym Symp 42:591