

# INORGANIC AND ORGANIC BLENDED, GRAFTED AND CROSSLINKED MATERIALS: THE CASE OF POLY(ETHYLENE OXIDE) AND (4-BENZOYLPHENOXY)<sub>-0.5</sub>(METHOXYETHOXY ETHOXY)<sub>-0.5</sub>PHOSPHAZENE COPOLYMER

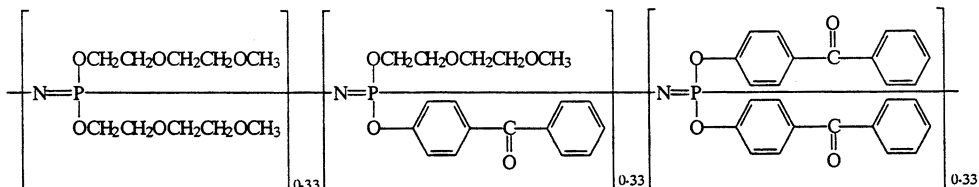
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**Abstract** In this paper we describe the formation of blends between poly(ethylene oxide) and a phosphazene copolymer almost equimolarly substituted with methoxyethoxyethoxy- and benzophenone- residues, together with the grafting and the crosslinking processes taking place between these substrates upon selective light irradiation of the benzophenone moieties present in the phosphazene system.

## INTRODUCTION

The synthesis of poly[bis(methoxyethoxyethoxy)phosphazene], MEEP<sup>1</sup> marked an important date in the modern phosphazene research because it opened the possibility of using phosphazene polymers, that are intrinsically good insulating materials<sup>2</sup>, as efficient ionic conductors in the construction of "lightweight rechargeable lithium batteries"<sup>3</sup>. In the frame of this work we recently prepared a new phosphazene copolymer almost equimolarly substituted with benzophenone and ethylene oxide units (BzMEEP)<sup>4</sup> having the following chemical structure:



that possesses at least two important characteristics, *i.e.* it is able to efficiently crosslink upon irradiation due to the presence of benzophenone residues in its chemical structure, and it is able to form blends with PEO macromolecules due to the good chemical affinity existing between the methoxyethoxyethoxy phosphazene substituents and the PEO skeletal units. In this paper we report the blending processes taking place between PEO and BzMEEP, the related crosslinking and grafting reactions undergone by these substrates upon light exposure, together with DMTA and DSC analyses.

## EXPERIMENTAL

The (4-benzoylphenoxy)<sub>-0.5</sub>(methoxyethoxyethoxy)<sub>-0.5</sub> phosphazene copolymer used in this work was prepared according to literature<sup>4</sup>. Poly(ethylene oxide) macromolecules of molar masses of 10<sup>5</sup>, 4x10<sup>5</sup>, 10<sup>6</sup>, and 4x10<sup>6</sup> Dalton (Aldrich), respectively, were used as received. PEO/BzMEEP blend films were prepared by casting from CH<sub>2</sub>Cl<sub>2</sub> solutions on Petri disks at a concentration of 10-20 mg/ml of polymer, depending on the PEO molar mass. A high pressure Hg lamp of 150 W and appropriate cut off filters were used for the selective light irradiation of the polymer blends. Thermal characterization and dynamic mechanical thermal analysis in shear configuration were performed by using a Differential Scanning Calorimeter Mettler DSC30 and a PL-DMTA MkII instrument (Polymer Laboratories / Rheometrics) in the range -100/+150°C with a heating rate of 10°C/min and 3°C/min, respectively.

## RESULTS AND DISCUSSION

Initial measurements of the BzMEEP glass transition temperature, T<sub>g</sub>, by DSC showed a value of -20°C for the dry polymer, that is remarkably influenced by the presence of moisture in the system (T<sub>g</sub> of the wet polymer: -27°C) The addition to BzMEEP of variable amounts of poly(ethylene oxide), PEO, to form blend evidenced the progressive shifting of the T<sub>g</sub> value for the virgin BzMEEP towards -50°C in dependence on the final composition of the polymer mixture (Figure 1). Almost the

same  $T_g$  values were found from the onset temperature of the shear storage modulus ( $G'$ ) curve by DMTA, and shown in Figure 2.

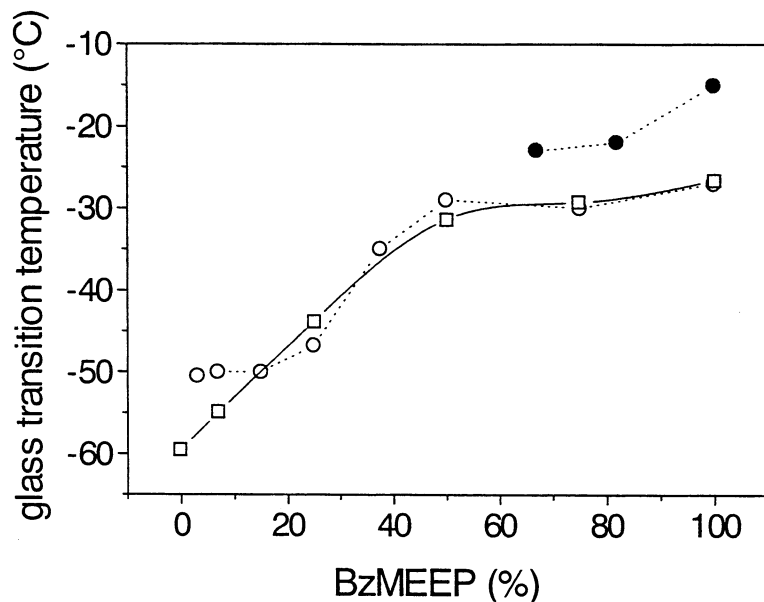


FIGURE 1.  $T_g$  of BzMEEP/PEO blends measured by DSC (circle) and by DMTA (square). Full circles refer to samples after 30 mins of irradiation and  $\text{CHCl}_3$  extraction.

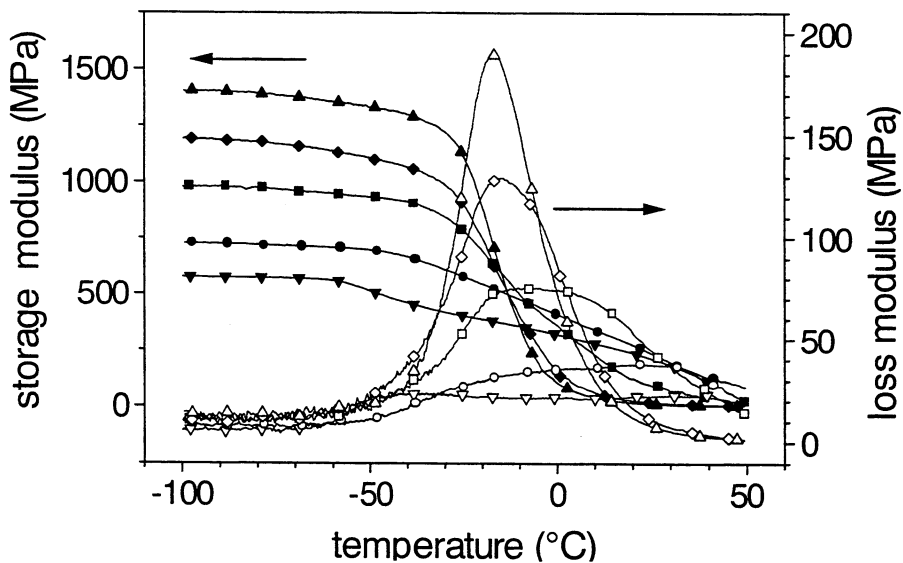
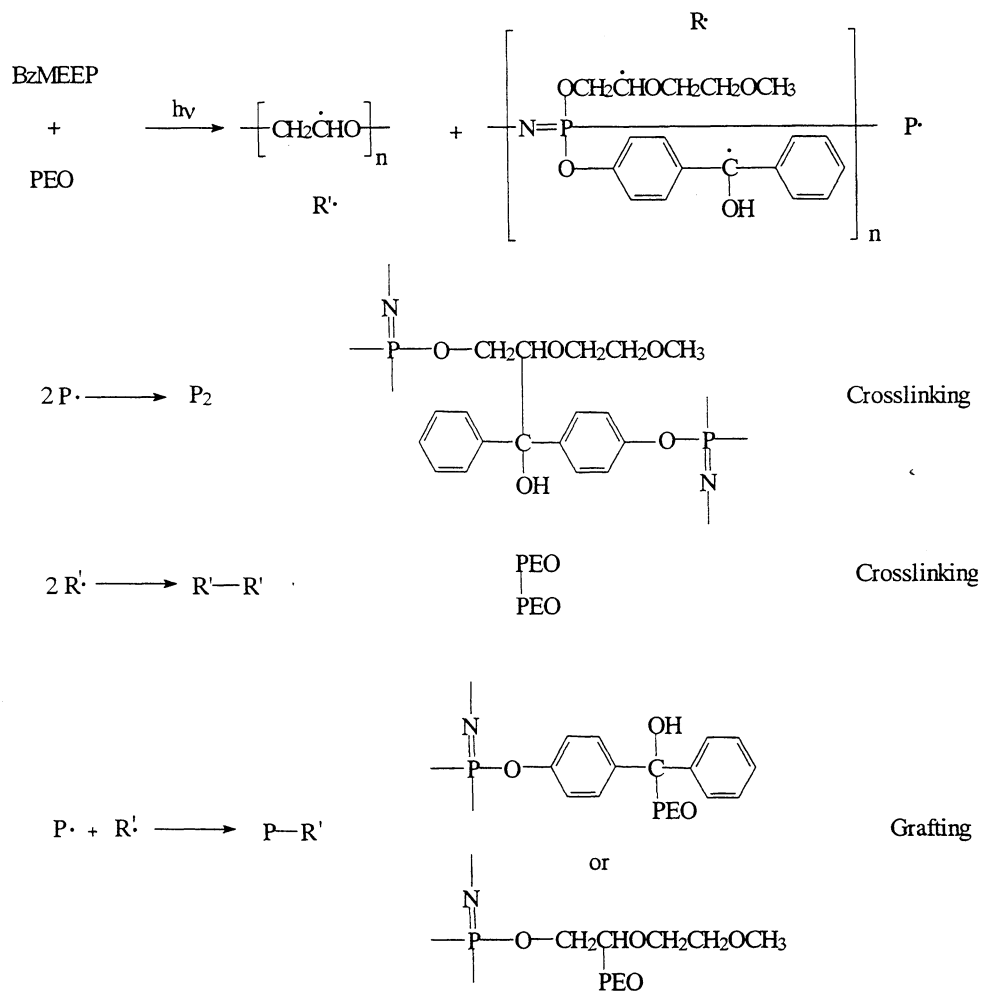


FIGURE 2. Shear storage modulus (full symbols) and loss modulus (empty symbols) of BzMEEP/PEO blends containing 0(▼), 25(●), 50(■), 75(◆) and 100(▲) % of BzMEEP, respectively.

Moreover from these DMTA measurements<sup>5</sup>, BzMEEP showed in the glassy state a shear modulus higher than the semicrystalline PEO, and an approximate rule of mixture could be observed for BzMEEP/PEO blends at low temperature below  $T_g$  of POP. On the other hand, at room temperature above  $T_g$ , an opposite tendency was found and PEO revealed a higher stiffness than BzMEEP. Moreover the  $G'$  decay resulted proportional to BzMEEP fraction in the blend, by two orders of magnitude in the case of pure BzMEEP and less than one order of magnitude in the case of pure PEO. These facts could be easily accounted for by the onset of chemical interactions between BzMEEP and PEO due to the chemical similarity of the ethylene oxide units contained in both these substrates. The presence of these interactions is a quite important fact for the BzMEEP/PEO system because it allows the occurrence of photochemical reactions between the benzophenone groups present in BzMEEP and the ethylene oxide units of both BzMEEP and PEO macromolecules, that could not be possible if the two polymers were segregated in different microdomains.

According to the reported Scheme, the irradiation of BzMEEP/PEO blends with light of wavelength longer than 250 nm, in such a way that only the selective excitation of the benzophenone residues in BzMEEP is obtained, brings about the formation of benzophenone excited triplets<sup>6</sup>. These species are able to abstract hydrogen radicals from both the methoxyethoxyethoxy phosphazene substituents and the PEO macromolecules to form highly reactive macroradicals, whose coupling reactions lead to the grafting of PEO onto BzMEEP and to the concurrent final crosslinking and insolubilization of the overall system. These processes were found to depend on at least three different experimental parameters, *i.e.* the irradiation time, the percentage of BzMEEP (*i.e.* of benzophenone units) in the blend and on the molar mass of the PEO macromolecule exploited for the blending experiments. In fact, the longer the time of the light exposure of the blend, the higher the concentration of benzophenone photosensitizer in the polymer mixture, and the more elevated the molar mass of PEO, the higher the final entity of the grafting process of PEO onto BzMEEP and the degree of the observed crosslinking. This fact could be also proved by swelling experiments from which it appears that the highest crosslinking yield of the BzMEEP/PEO blends is

obtained for the shortest irradiation time and for the lowest content of benzophenone concentration in the polymer mixture.



Scheme

The effect of both crosslinking and grafting is well evident from DSC analysis. First of all after irradiation, the  $T_g$  increased of about 10-15°C in the case of materials with BzMEEP percentage higher than 50%, whereas in the other cases it was not possible to determine the inflection point (Figure 1). Furthermore, the endothermal peak related to the melting of crystalline PEO at about 70°C, after 30 minutes of irradiation and extraction with chloroform, was found to decrease especially in the second DSC scan, as a

consequence of the reduced crystallizability of PEO units (see Figure 3).

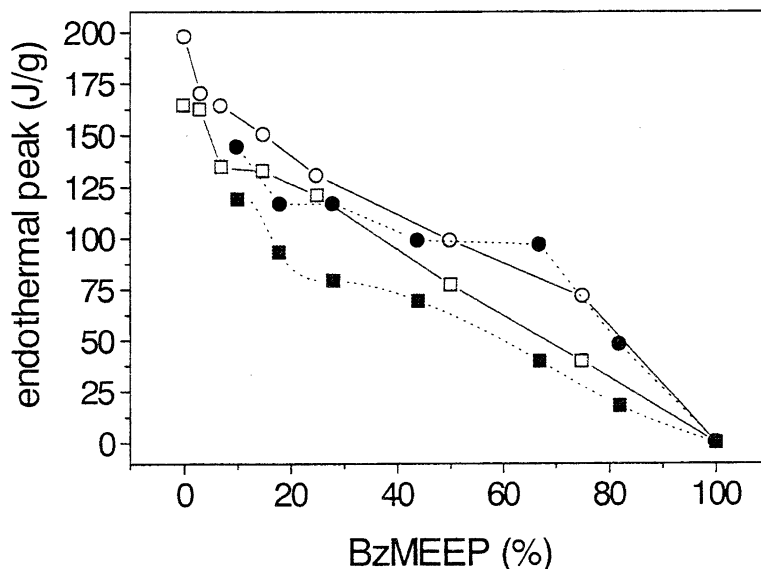


FIGURE 3. Endothermic peak of crystalline phase in BzMEEP/PEO blend measured in the first (circle) and in the second (square) DSC scan, respectively. Empty and full symbols refer to initial samples and samples after 30 mins of irradiation and chloroform extraction.

Additional experiments on the thermal and dynamical-mechanical characterization of these new materials together with measurements of their ionic conductivity characteristics are presently under way.

#### REFERENCES

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