

Grafting onto Preformed Polyester Network Using Thermolabile Azo Groups

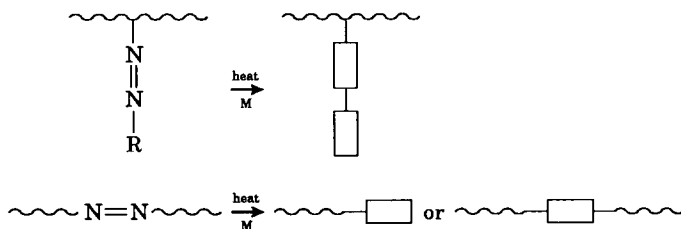
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Synopsis

Polycondensation of 4,4-azo-bis(cyanopentanoyl chloride) and *o*-phthalyl chloride between polyethylene glycol with addition of glycerine leads to polyester networks containing thermolabile azo groups. The networks have been characterized in terms of their swelling in benzene, chlorobenzene, and methacrylonitrile. Grafting of methacrylonitrile onto these preformed networks was then achieved by thermal decomposition of $-N=N-$ groups in the presence of methacrylonitrile.

INTRODUCTION

In recent years, the synthesis of novel polymeric materials with specific properties has become an attractive field of polymer science. Block and graft copolymers that provide a combination of the physical properties are the most suitable materials for various purposes. Polymers containing thermolabile azo functions in the main or side chain are especially suitable for the preparation of block and graft copolymers, respectively.¹



Previously, we have prepared polymers containing an azo linkage in the main chain by means of condensation,^{2,3} cationic,⁴⁻⁶ and anionic insertion⁷ polymerization techniques. Several other types of azo polymers have been described in the literature.¹ Recently, Nuyken et al.⁸ prepared poly(methylmethacrylate)/butanediol-1,4-dimethacrylate networks containing thermolabile azo functions. Upon heating, crosslinked polymer underwent side-chain scission leading to generation of free radicals that are capable of initiating polymerization of vinyl monomers.⁹

In this work, we describe synthesis of polyester networks containing poly(ethyleneglycol) segments and thermolabile $-N=N-$ linkage that provides appropriate functionality for the subsequent grafting reactions.

EXPERIMENTAL

Materials

Azobiscyanopentanoyl chloride (ACPC) was obtained from the corresponding diacid (Fluka) as described previously. *o*-Phthalyl chloride (PC) was prepared by reacting phthalic anhydride with phosphorous pentachloride according to the described procedure.¹⁰ Commercial-grade PEG-400 (molecular weight 400) supplied by Hoechst and glycerine (Merck) were used as purchased. Methacrylonitrile (MAN), trichloroethylene, triethylamine, and other solvents were purified according to the conventional drying and distillation procedures.

Synthesis of Crosslinked Polyesters Containing Azo Groups

A four-necked flask with a calcium chloride drying tube, magnetic stirrer, reflux condenser, and a thermometer was charged with PEG-400, glycerine, and triethylamine in the amounts given in Table I. As a solvent 50 mL of thichloroethylene was added to this mixture. After PEG-400 was dissolved in the solvent at 30°C with stirring, the flask was cooled to 0°C and an equivalent amount of ACPC + PC was added slowly so that the temperature of the reaction did not exceed 5°C. The mixture was continuously stirred at 30°C for 48 h to complete the polycondensation. At the end of this period the reaction mixture was taken into chloroform. The insoluble portion was filtered off and then washed successively with chloroform, water, and alcohol. Crosslinked polyester thus separated was dried in a vacuum oven and designated as (CPE)*.

Swelling Experiments

Weighed amount of the polymer pearls (CPE)*, ca. 250 mg, and a given solvent were placed into a sample bottle. The sealed sample was kept at 5°C for 7 days. The solvent was then decanted, the pearls superficially dried with tissue, and then reweighed to determine their swollen weight and thus 1/*Q*.

Grafting Experiments

Known amounts (0.1–0.3 g) of the pearl CPE* (passing from 25 mesh/cm sieve) were weighed into a reactor. After adding a given amount of MAN (Table

TABLE I
Preparation of CPE* by Polycondensation at 30°C

Series	ACPC (g)	PC (g)	ACPC/ACPC + PC (mol ratio)	PEG (g)	Glycerine (g)	Triethylamine (g)	Product ^a (g)
CPE ₁ *	2.6	—	1	0.6	0.4	2	0.9
CPE ₂ *	1.52	2.27	0.43	1.2	0.8	2	1.37
CPE ₃ *	0.34	1.97	0.11	0.4	0.6	2	0.21
CPE ₄ *	0.25	3.07	0.05	1.2	0.8	2	0.30
CPE ₅	—	6.1	0	2.25	1.5	6	1.9 ^b

^a Insoluble product.

^b Does not contain labile azo groups.

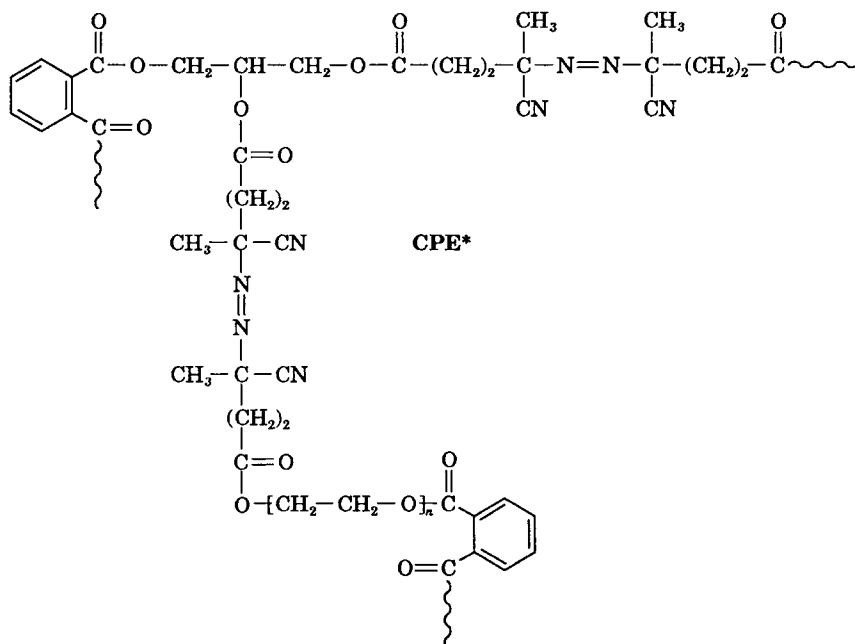
III), the mixture was degassed by several freeze-thaw cycles. This procedure improved the swelling of the crosslinked polymer. The reactor was then filled with nitrogen and immersed into a constant-temperature bath. During the grafting, the mixture was vigorously stirred to obtain optimal phase dispersity. At the end of the reaction hydroquinone was added to the system.

The homo-PMAN was separated from the reaction content by dissolving in acetone. PMAN graft was determined directly from the weight increase of the pearl polyester. Percent grafting was calculated as the percent increase in weight over the original weight of the crosslinked polymer.

$$\text{Percent grafting} = \frac{\text{wt. grafted sample} - \text{wt. sample}}{\text{wt. sample}} \times 100$$

RESULTS AND DISCUSSION

The results of copolycondensation of ACPC-PC/PEG-400 using glycerine as trifunctional crosslinking agent are summarized in Table I. The potential grafting positions, $-\text{N}=\text{N}-$ groups, in CPE* may be arranged approximately by the mole ratio of (ACPC/ACPC + PC) in the feed composition. For all experiments the ratio of PEG-400 to glycerine was adjusted so as to achieve crosslinking as well as good swelling properties, which are important requirements for the subsequent grafting reactions. Although it is difficult to give an exact composition of CPE*, a representative structure may be written as follows:



As can be seen from Table II, for swelling polyester networks that contain azo groups (CPE₁* and CPE₃*), MAN is a better solvent than benzene or chlorobenzene. Furthermore, MAN provides several other advantages in the grafting

TABLE II
 Swelling Properties of CPE* ^a

Swelling solvent	1/Q Values for		
	CPE ₁ *	CPE ₃ *	CPE ₅
Benzene	0.37	0.50	0.43
Chlorobenzene	0.25	0.51	0.29
MAN	0.23	0.46	0.40

$$^a 1/Q = \frac{\text{dry weight (g)}}{\text{swollen weight (g)} - \text{dry weight (g)}}$$

experiments. These include low polymerizability of MAN at the maximum temperature at which the experiments were carried out (80–90°C), and the boiling point of MAN is above the decomposition temperature of azo groups. The recipes and results of grafting of MAN onto crosslinked polyesters are summarized in Table III. Percentage grafting onto crosslinked surface was not efficient when a high azo-containing preformed network is used. This is expected since upon heating CPE₁* becomes soluble in MAN due to decomposition of azo groups that are the only linking groups in the network. Addition of MAN to the polymeric radicals results in block and graft copolymerization as well as homopolymerization in homogenous phase. In contrast, experiments with crosslinked polymer having 0.1 ACPC/ACPC + PC mol ratio led to high percentage grafting on the crosslinked surface. The graft polymerization takes place within the polymer particles, and homopolymerization can only be initiated by the radicals that have diffused out of these particles.

IR spectrum of the grafted polymer shows an increased CN band, at 2240 cm⁻¹ indicating grafted MAN chain, in addition to characteristic ester peak at 1730 cm⁻¹ (Fig. 1). It should be pointed out that the weak absorption at 2240 cm⁻¹ in the initial crosslinked polymer is due to the CN group present in the azo initiator. It is noteworthy that lower —N=N— content greatly reduces the percentage grafting, although there is no homopolymer formation due to the limited diffusion out of the polymer pearls (Table III, run 4).

 TABLE III
 Grafting of MAN onto the Crosslinked Polyester at 80°C in Bulk

CPE	Weight CPE (g)	MAN (g)	Reaction time (h)	Soluble (g)	Insoluble (g)	Percentage grafting ^a (%)
CPE ₁ *	0.125	6	7	0.08	0.050	—
CPE ₂ *	0.300	6	24	0.07	0.23	—
CPE ₃ *	0.148	8	24	0.026	0.202	42.3
CPE ₄ *	0.147	8	24	—	0.157	6.7

^a On the crosslinked surface.

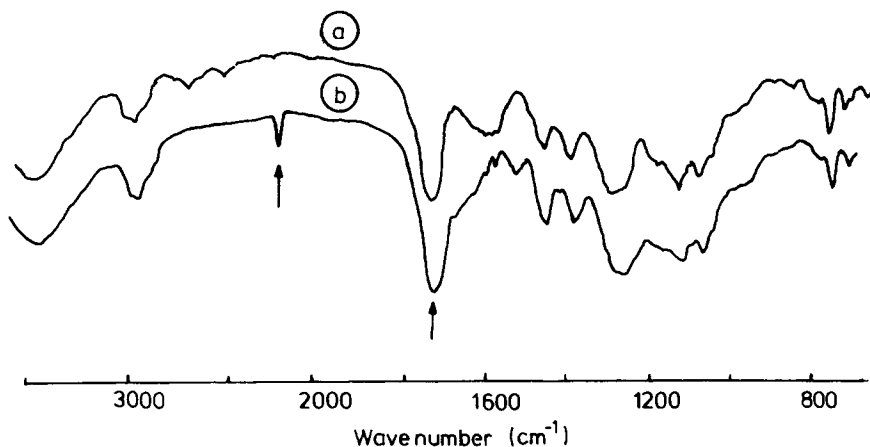


Fig. 1. IR spectra of crosslinked polyester (CPE_3^*). (a) before and (b) after grafting methacrylonitrile.

CONCLUSION

Grafting of MAN could be accomplished successfully onto the preformed polyester network containing poly(ethyleneglycol) segment and thermolabile $-\text{N}=\text{N}-$ linkage. Since MAN is a good solvent in respect of swelling the network, grafting reaction was carried out in the presence of MAN without using any other solvent. More importantly, it should be stated that the percentage grafting onto the crosslinked surface depends mainly on the azo content of the network.

References

1. O. Nuyken and R. Weidner, *Adv. Polym. Sci.*, **73-74**, 145 (1986).
2. Y. Yagci, U. Tunca, and N. Bicak, *J. Polym. Sci. Polym. Let. Ed.*, **24**, 49 (1986).
3. Y. Yagci, U. Tunca, and N. Bicak, *J. Polym. Sci. Polym. Let. Ed.*, **241**, 49 (1986).
4. Y. Yagci, *Polym. Commun.*, **26**, 7 (1985).
5. A. Akar, A. C. Aydogan, N. Talinli, and Y. Yagci, *Polym. Bull.*, **15**, 293 (1986).
6. G. Hizal and Y. Yagci, *Polymer*, **30**, 722 (1989).
7. Y. Yagci, Y. Menceloglu, B. Baysal, and A. Gungor, *Polym. Bull.*, **21**, 259 (1989).
8. O. Nuyken, L. Dyckerhoff, and R. Kerber, *Angew. Makromol. Chem.*, **143**, 1 (1986).
9. O. Nuyken, L. Dyckerhoff, and R. Kerber, *Angew. Makromol. Chem.*, **143**, 11 (1986).
10. A. H. Blatt, *Organic Syntheses*, Wiley, New York, 1963, Vol. 2, p. 528.

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