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THE MODIFICATION OF POLY (ETHYLENE TEREPHTHALATE) FIBERS WITH GRAFT COPOLYMERIZATION: A REVIEW

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ABSTRACT

The superior properties of poly (ethylene terephthalate) fibers are due to the high degree of orientation and structural order of macromolecular chains. This excellent characteristics are, however, also the source of some negative features such as nearly complete water repellency, difficulty in dyeability, and formation of static charge etc. One of the ways to improve these undesirable features is grafting of various monomers upon the poly (ethylene terephthalate) fibers by graft copolymerization. The most common grafting methods namely using ionising irradiatiaon and chemical initiators were briefly mentioned in the first part. The second is mainly dwelled upon the changes observed in the properties of the poly (ethylene terephthalate) fibers as a result of grafting process.

INTRODUCTION

Among the synthetic origined fiber groups, poly (ethylene terephthalate) (PET) fibers have an important place in the textile industry today. This is largely due to superior physical and chemical properties of PET fibers. They are resistant against many chemicals and dimensionally stable. They are also unaffected by mildew and mooths. PET fibers have some undesirable properties besides with these desirable ones. Among these, one can list the low moisture regain, tendecy to pill, formation of static charge, and difficulty in dyeability.

The moisture regain value of PET fibers at 25 °C and 65 % relative humudity is 0.40 %. The moisture regain values of silk and cotton are about 11 %, and nylon-6 4.5 % (Smith 1969). The lack of chemically active groups alongside the PET macromolecular chains, makes it impossible to be dyed with acidic, basic and other type of dyes. PET fibers can only be dyed with disperse dyes. The disperse dyes are not effective on the active groups in the structure, since they enter the structure physically. The crystalline structure of PET also makes dyeing with disperse dyes an expensive process. As a result, these undesirable properties of PET fibers have a limiting role in the use of PET fibers in some textile applications. For instance, the moisture regain value of PET fibers show that they are not appropriate for underwear production.

There are extensive studies to overcome these undesirable features of PET fibers and give them some desirable properties.

One of the research area is the addition of some antistatic, hydrophilic or other compounds which ease the dyeing process (these chemicals can be added during transesterification or polycondensation processes, depending on their chemical role and structure). However, the applicability of this technique is limited since it causes the loss of some fiber properties.

Another alternative is grafting of a monomer (or monomers) upon the PET fiber by graft copolymerization. This enables one to give new properties to PET fibers depending on the monomer (or monomers) grafted upon it.

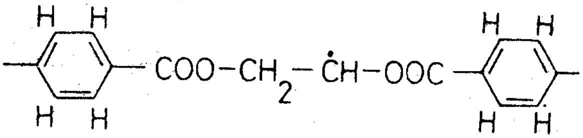
A GENERAL OUTLOOK OF GRAFT COPOLYMERIZATION UPON PET FIBERS

The most common methods used in grafting of various monomers upon PET fibers are the employment of ionising radiation and chemical initiators.

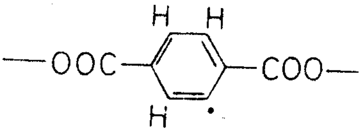
The decision of which graft copolymerization method is suitable generally depend on the ease of application, the reproducibility of the experiments ,the effect of the method on basic fiber properties and the probability of obtaining the expected properties as a result of the grafting process.

The ionising radiation (γ -rays, x-rays etc.) is known to give R_1 and R_2 type radicals when interacted with the PET fibers (Campbell 1967).

These radialic active sites which are considered as side chain attachment points of the grafted monomer, can be formed chemically in the presence of benzoyl peroxide (Lokhande 1984. Okoniewski 1981, Saçak 1989, Shalaby 1978, Okoniewski 1984), hydrogen peroxide (Hebeish 1982, Hebeish 1978), azobisisobutyronitrile (Tsuzuki 1971, Sakurada



(R_1)



(R_2)

1970), potasium persulfate (Yamauchi 1972), or cerium ion (Pradhan 1982, Suzuki 1972).

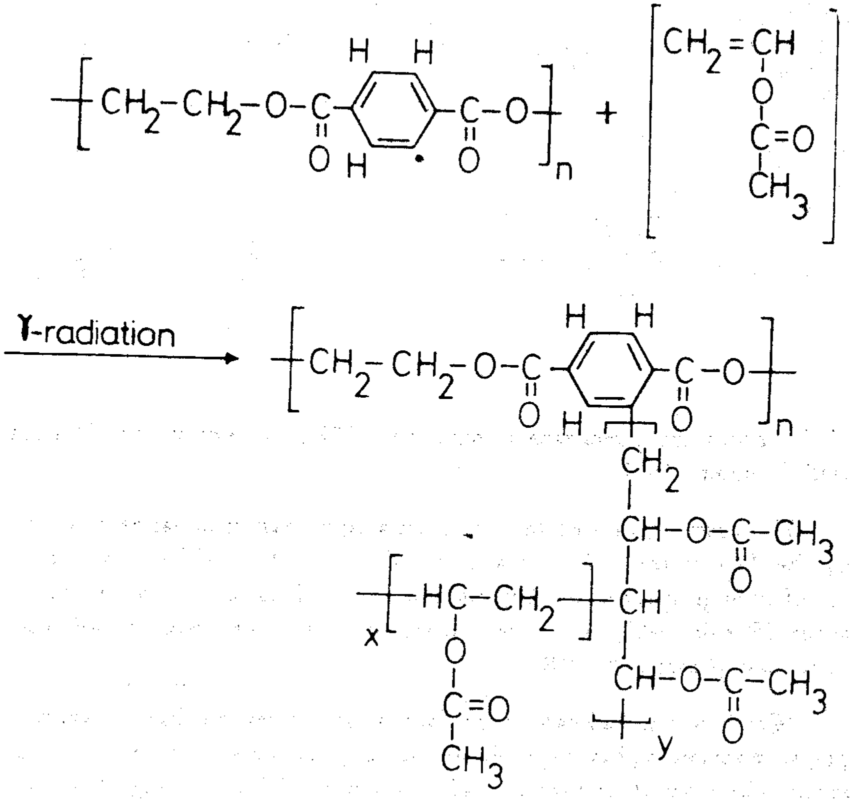
The grafting carried out with ionising radiation is easire to control by the dose of the radiation applied. However, the PET fibers loose some of their properties at radiations above 5 Mrad, and crosslinking can occur (Potnis 1969). At lower doses, however, the yield of radicals is very low (Campbell 1970).

Which of the radicals mentioned above is responsible for graft copolymerization highly depends on the applied dose. For instance, in a study where vinyl acetate is grafted upon PET fibers the grafting sites were shown to be R_2 type radicals and the following structure was proposed for the grafted PET fiber (Faterpeker 1980).

Some of the monomers used in the grafting studies with ionising radiation are styrene (Sakurada 1973, Vlagio 1973, Memetea 1979, Mikhailov 1962), acrylic acid and methacrylic acid (Rao 1972, Kale 1975, Bonnefis 1971, Blin 1969, Matsuzaki 1972), acrylamide (Yamauchi 1972) 2-methyl-5-vinylpyridine (Hebeish 1978), methyl methacrylate (Matsuzaki 1972), and acrylonitrile (Yamauchi 1972, Kale 1975).

Although it is difficult to control the polymerization conditions in grafting carried out with chemical initiators, the degradation of the main polymer remains at a very low level. They are easy to apply and do not need any special apparatus.

Whether one uses ionising irradiation or chemical initiators, there occurs the homopolymer of the grafted monomer, in the polymerization



medium. The most common procedure used to remove the homopolymer from the grafted fiber is the extraction of it with a suitable solvent. The removal of the homopolymer is a time and solvent consuming process.

Generally PET fibers are used in grafting studies, but in the literature there are also grafting studies on the PET fabric using various monomers (Hebeish 1982, Okada 1970T).

The highest grafting yields seem to be obtained around the glass-transition temperature of PET fiers (80 °C). The studies in the literature emphazise that the graft yield decreases in grafting processes carried out above or below this temperature (Vlagiu 1973, Schamberg 1970, Rao 1979).

THE PROPERTIES OF GRAFTED PET FIBERS

a) DYEABILITY

The PET fibers can be dyed with various dyes depending on the chemical properties of the monomer grafted upon them. The fibers grafted with a monomer having acidic properties are expected to have improved dyeability with basic dyes and vice versa.

The theoritical structure of PET macromolecules is as follows:

$$HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}(CO\text{-}\phi\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}O)_n\text{-}CO\text{-}\phi\text{-}COO\text{-}CH_2\text{-}CH_2\text{-}OH$$

However, the commercial PET produced by dimethyl terephthalate (or terephthalic acid) and ethylene glycol does not have this structure. By hydrolysis and thermal decomposition and oxidation of PET during its synthesis and melt spinning, carboxylic groups are formed as end groups. Although there are significant number of COOH groups, they do not enable the fiber to be dyed with all basic dyes. In addition to high crystallinity and water repellency, the very low acidity of the carboxylic groups of PET is responsible for this behavior.

Suzuki et al. (1972) reported that the grafting of acrylic acid upon PET fibers increased their dyeability with basic dyes while the grafting with acrylamide increased the dyeability with acidic dyes. In both situations the dyeability was reported to increase with the graft yield.

The grafting of acrylamide-styrene mixture upon PET fibers was reported to increase the absorption of acidic dyes. The dye absorption at 38 % graft yield (7.8 % polystyrene and 30.2 % polyacrylamide) was 46 mg dye / g fiber while it increased to 63 mg dye / g fiber at a graft yield of 55 % (17.5 % polystyrene and 37.5 % polyacrylamide) (Jones 1968).

The dyability of the PET fibers with acidic dyes was observed to increase when they are grafted with acrylamide using benzoyl peroxide. The dyeability of ungrafted PET fiber was nil but it increased to 18 mg dye / g fiber when they are grafted with 22 % acrylamide. The dyeability showed a decrease at higher grafting values (Saçak 1986).

In the studies carried out on the grafting of PET fibers with acrylic acid, it was reported that the dyeability increases with basic dyes (Kale 1975, Kim 1984, Schamberg 1970, Ohguchi 1984).

Okada et al. (1968) reported that although there was a moderate increase in the dyeability of PET fiber grafted with 15 % 4-vinylpyridine, there observed no improvement in the dyeability of the fiber grafted with more than 20 % 2-vinylpyridine. The grafting of these two monomers together caused a moderate increase in the tendecy of the fiber towards acidic, disperse, basic and direct dyes.

Hebeish et al. (1982) examined the grafting of various monomers upon the PET fibers and reported that the dyeability of the fibers grafted with methyl methacrylate or acrylic acid-styrene mixture with disperse dyes showed an increase. They also claimed that the dyeability of the PET fibers grafted with glycidyl methacrylate, with direct and reactive dyes, was improved.

The microscopic examination of the fiber following the dyeing of the grafted fibers give us an idea about the extention of the grafting. The degree of the extention of the dyeing from the surface to the center of the flament shows that the grafting process approches to the flament center. For instance, when the flament corss-section of the fiber grafted with 22 % acrylamide was examined under microscope after being dyed with acidic dyes, dyeing process was found to extend throughout the whole flament cross-section. Considering the fact that the molecules of the acidic dyes can only interact with the -NH_2 groups of acrylamide it can suggested that the grafting process must be extended towards the center of the flament (Saçak 1989).

Similarly Okada and Sakurada (1970) basing upon their microscopic studies on the PET fibers grafted with acrylic acid, stated that grafting could be homogenously carried out throughout the whole flament cross-section at 16.3 % grafting.

There are other studies which also state that the grafting process was carried out homogenously throughout the whole flament cross-section (Bonnefis 1971, Kim 1984, Okada 1971).

b) MOISTURE REGAIN VALUE

Moisture regain is generally related to the hydrophilic structure of the fiber. The moisture regain value of polyester fibers having hydrophobic character is quite low. The moisture regain value of PET fibers can be increased by grafting various monomers upon PET fibers which give hydrophilic character to them. In Table I the mositure regain values of PET fibers grafted with different monomers are tabulated with respect to the grafting ratio.

Table 1. The moisture regain values of the PET fibers grafted with various monomers

monomer	graft yield (%)	moisture regain (%)	reference
acrylic acid	0.00	0.40[a]	Bonnefis 1971
(65 % relative humudity, 25°C)	10.0	2.75[a]	
	30.0	3.80[a]	
glycidyl methacrylate	00.0	0.39	Hebeish 1983
(65 % relative hamudity, 25°C)	16.0	0.76	
	46.1	1.95	
	149.8	2.04	
acrylic acid	00.0	0.60	Kale 1975
(75 % relative humudity, 30°C)	10.0	2.00[a]	
	25.6	4.46	
methyl methacrylate[b]	00.0	0.00	Pradhan 1982
	15.0	1.85	
	25.0	2.25	
	30.0	2.50	
acrylamide (65 % relative humudity, 20°C)	00.0	0.42	Saçak 1989
	19.1	1.89	
	28.3	1.96	
	41.7	3.92	
acrylamide-methacrylic acid	00.0	0.42	Saçak 1986
(65 % relative humudity, 20°C)	25.0	1.56	
	57.6	2.83	

a- The approximate graft yield and moisture regain values were obtained from the graft yield-moisture regain plots given in literature.

b- The conditions of the moisture regain experiments have not been stated.

The extention of the fiber structure following the grafting process contributes to the increase in the moisture regain to a certain extent. However, the moisture regain value of the fiber was observed to decrease after a certain grafting value due to blocking of the porous structure of the fiber (Kale 1975).

It was also stated that the conversion of the acid groups upon the monomer grafted onto PET fibers, into the metal salts such as sodium, increased the moisture regian value (Okada 1970).

The conversion of the acid groups of the PET fiber grafter with acrylic acid, into the sodium or calcium salts, enabled the fiber to have a moisture regain value higher then 10 %, in a medium having a relative humudity of 65 % (Suzuki 1972).

Similiarly Ohguchi and Yasamura (1981) converted the acid groups of the PET fibers grafted with methacrylic acid, into the sodium salts, and obtained fibers having improved moisture regain value. However subjecting this fiber to normal washing procedure caused the sodium ions in the structure to be replaced with calcium ions which in turn decreased the moisture regain value of the fiber.

c) OTHER PROPERTIES

Static charges are generated when moving fibers are deteched from the contacting surface. As in many synthetic origined fibers, there observed to be static charge on the PET fibers. However, many studies indicate that the antistatic properties of PET fibers could be improved by grafting various monomers upon them (Kale 1975, Bonnefis 1971, Maeda 1973, Igeta 1975, Okaniewski 1981).

Tsuzuki et al. (1971) obtained a fire resistant fiber, by grafting the PET fiber with styrene and keeping it in aqueous bromine solution under sunlight for three hours. It was also reported that a flame resistant PET fabric was obtained by grafting bromostyrene directly upon the PET fabric (Mey-Marom 1983).

Hebeish et al. (1982) investigated the soiling property of the PET fabric grafted with glycidyl methacrylate, methyl methacrylate and acrylic acid-styrene mixture. They reported that the fibers grafted with methyl methacrylate improved both aqueous and nonaqueous soil removal properties. The grafting of vinyl acetate upon the PET fiber improved its soiling resistance (Magat 1966).

Generally it was observed that mechanical properties of the PET fibers weaken following the grafting process. Therefore, care must be taken not to deteriorate the mechanical properties of the fiber while it is being grafted to improve its other properties.

The grafting of acrylic acid and methacrylic acid upon the PET fibers by the help of benzoyl peroxide caused little decrease in their strength (Toray Industries, Inc. 1984). Kale et al. (1975) reported that when the fibers are grafted with acrylic acid up to 22.4 % by the help of x-rays the strength decreased by 35 %. Ohguchi and Yasamura (1981) investigated the grafting of acrylic and methacrylic acid upon the PET fiber and reported that the modules, tenacity at break and elastic recovery of the grafted fiber decreased whereas elongation at break increased with increasing grafting value. Faterpeker and Potnis (1980) stated that the tensile strength and percentage elongation of the PET fiber increased up to 22 % grafting with vinyl acetate and than showed a sharp decrease. Some studies report that the strength of the PET fiber is not affected by grafting (Okada 1970, Lits 1984).

Faterpeker and Potnis (1980) also investigated the thermal behaviour of the PET fibers grafted with poly (vinyl acetate) and poly (vinyl alcohol). They noted that the melting temperature and heat of fusion of PET fibers were not affected by grafting. They also stated that grafting with poly (vinyl acetate) did not affect the thermal stability of PET fiber.

It was stated that the glass-transition temperature of the PET fibers grafted with acrylic acid decreased with the increasing grafting ratio (Kim 1984). It was also reported that the fiber density of the grafted fibers decreased and the fiber radius increased with the increasing grafting yield (Saçak 1989, Ohguchi 1981).

CONCLUSION

The polyester fibers which have a prominent place among the synthetic origined fibers, have found new areas of application since their first production in 1950s. This prominent place of PET fibers among synthetic fibers is largely due to their superior physical and mechanical properties. The grafting studies of PET are therefore directed to improve the weaker sides of PET such as difficulty in dyeability, low moisture regain, and high pilling. The studies conducted in this field have an important place in literature, in last twenty years.

Although the results of the studies of grafting different monomers upon the PET fibers are very promising, they create some important problems as well.

Some of the important problems to be solved in the application of the graft copolymerization process are as follows; minimising the homopolymer formation which causes excess loss of material (solvent, monomer etc.), the complete removal of the homopolymer from the fiber, continuity of production and maintaining high production capacity. Another important point is, keeping the number and lengths of the side chains which are the most important factors in the characterization to graft copolymers, under control. In fact there is no graft copolymer type synthesized by controlling these factors yet.

Most of the problems mentioned above will be solve in future, if we take the intensive studies carried out in this area into account.

REFERENCES

BLIN, M.F., CANDAN, R., GAUSSENS, G., LEMAIRE, F., and PAOLI, D., Fr. Pat., 2, 045, 261 (1969), Chem. Abstr. 76, 15692v (1972).

BONNEFIS ,J.C. and PUIG, J.R., 1971, J. Appl. Polym. Sci., 15, 553.

CAMPBELL, D. and TURNER, D.T., 1967. J. Polym. Sci., Part A-1 5, 2199.

CAMPBELL, D., MONTEITH, L.K. and TURNER, D.T., 1970. J. Polym. Sci., Part A-1 8, 2703.

FATERPEKER, S.A. and POTNIS, S.P., 1980. Angew. Makromol. Chem., 90, 69.

HEBEISH, A., SHALABY, S.E. and BEYAZEED, A.M., 1978. J. Appl. Polym. Sci., 22, 3335.

HEBEISH, A., SHALABY, S.E., and EL-SHAHID, M.F., 1978. Angew. Makromol. Chem., 66, 139.

HEBEISH, A., SHALABY, S. and BAYAZEED, A., 1982. J. Appl. Polym. Sci., 197.

HEBEISH, A., SHALABY, S.E. and BAYAZEED, A.M., 1982. J. Appl. Polym. Sci., 27, 3683.

HEBEISH, A., SHALABY, S., WALY, A. and BAYAZEED, A., 1983. J. Appl. Polym. Sci., 28, 303.

IGETA, K. and OHGUCHI, M., Jpn. Pat. 76 87, 592 (1975); Chem. Abstr. 84, 178879 m (1976).

JONES, M.H., Brit. 1, 129, 424 (1968); Chem. Abstr. 70, 20937j (1969).

KALE, P.D., LOKHANDE, H.T., RAO, K.N. and RAO, M.H., 1975. J. Appl. Polym. Sci., 19, 461.

KIM, H.D., KIM, D.L. and CHUN, T.I., Han'guk Somyu Konghakhoechi 21 (4), 233 (1984); Chem. Abstr. 102, 8128t (1985).

LITS, N.P., KORZHENEVSKII, A.B., RADUGINA, Zh. V. and GOLOVINA, I. Yu., USSR Pat. 1, 116, 101 (1984); Chem. Abstr. 102, 8220s (1985).

LOKHANDE, H.T., TELI, M.D., RAO, K.N. and RAO, M.H., 1984. J. Appl. Polym. Sci., 29, 1843.

MAEDA, S., Jpn. Pat. 73 12, 465 (1973); Chem. Abstr. 80, 49157 x (1974).

MAGAT, E.E. and TANNER, D., U.S. Pat. 3, 412, 176 (1966); Chem. Abstr. 70, 29995j (1969).

MATSUZAKI, K., KANAI, R. and MOTITA, N., 1972. J. Appl. Polym. Sci., 16, 15.

MEMETEA, T. and STANNETT, V., 1979. Polymer, 20, 465.

MEY-MAROM, A., RAJBENBACH, L.A. and LEVY, M., 1983. J. Appl. Polym. Sci., 28, 2411.

MIKHAILOV, N.V., TOKARERA, L.G., BRATCHENKO, T.D., KARPOV, V.L. and MALINSKII, Yu. M., Tr. Vses. Soveschc. Radiats. Khim. 2nd 1960, 589 (1962); Chem. Abstr. 62, 13296 g (1965).

OHGUCHI, M. and YASAMURA, T., Sen'i Gakkaishi, 37 (9), 354 (1981); Chem. Abstr. 96, 8015 m (1982).

OHGUCHI, M., Sen'i Hakkaishi, 40 (4–5), 147 (1984); Chem. Abstr. 101, 24925 k (1984).

OKADA, T., SUZUKI, Y., KOHDERA, K. and SAKURADA, I., JAERI 5018, 5 (1968); Chem. Abstr. 70, 116147c (1969).

OKADA, T. and SAKURADA, I., JAERI 5026, 56 (1970); Chem. Abstr. 74, 127283 c (1971).

OKADA, T. and SAKURADA, I., JAERI 5026, 46 (1970); Chem. Abstr. 74, 127284d (1971).

OKADA, T., KAJI, K. and SAKURADA, I., JAERI 5027, 50 (1971); Chem. Abstr. 76, 114582r (1972).

OKONIEWSKI, M., KOPROWSKA, J., SOJKA-LEDAKOWICZ, J., RAKOWSKI, W. and ZYSKA, D., Pol. Pat. 110, 224 (1981); Chem. Abstr. 96, 124483 m (1982).

OKONIEWSKI, M. and SOJKA-LEDAKOWICZ, J., Pr. Inst. Wlok., 29, 153 (1981); Chem. Abstr. 97, 111231 y (1982).

OKONIEWSKI, M. and SOJKA-LEDAKOWICZ, J., Pol. Pat. 122, 704 (1984); Chem. Abstr. 101, 56440 q (1984).

POTNIS, S.P., SHETTY, S.M., RAO, K.N. and PRAKASH, J., 1969. Angew. Makromol. Chem. 6, 127.

PRADHAN, A.K., PATI, N.C. and NAYAK, P.L., 1982. J. Appl. Polym. Sci., 27, 1873.

RAO, K.N., RAO, M.H., MOORTHY, P.N. and CHARLESBY, A., 1972. J. Polym. Sci., Polym. Lett. Ed., 10, 83.

RAO, K.N., RAO, M.H., LOKHANDE, H.T., MODY, N.R. and JOG, A.G., 1979. J. Appl. Polym Sci., 23, 2133.

SAÇAK, M., 1986. PhD Thesis. Ankara University, Ankara.

SAÇAK, M. and PULAT, E., 1989. J. Appl. Polym. Sci., 38, 538.

SAÇAK, M. and PULAT, E., 1989. Doğa Dergisi, 13, 246.

SAKURADA, I., SAKAGICHI, Y. and SAKAI, Y., Jpn. Pat. 70, 08, 756 (1970); Chem. Abstr. 73, 46562v (1972).

SAKURADA, I., IKADA, Y. and KAWAHARA, T., 1973. J. Polym. Sci., Polym. Chem. Ed., 11, 2329.

SCHAMBERG, E. and HOIGNE, J., 1970. J. Polym. Sci., Part A-1 8, 693.

SCHAMBERG, E. and HOIGNE, J., Ger. Offen. 2, 207, 178 (1970); Chem. Abstr. 74, 4347y (1971).

SHALABY, S.E., BAYZEED, A.M. and HEBEISH, A., 1978. J. Appl. Polym. Sci., 22, 1359.

SMITH, A.L., 1969. Encyclopedia of Polymer Science and Technology, vol. 6, pp. 593; John Wiley and Sons, Inc., New York.

SUZUKI, K., KIDO, I. and TANABE, N., Sen'i Gakkaishi 28(9), 343 (1972); Chem. Abstr. 77, 165878v (1972).

TORAY Industries, Inc., Jpn. Pat. 59, 124, 908 (1984); Chem. Abstr. 101, 153425 w (1984).

TSUZUKI, R. and MAETA, S., Jpn. Pat. 71, 29, 918 (1971); Chem. Abstr. 77, 50069q (1972)

VLAGIU, I. and STANNETT, V., 1973. J. Macromol. Sci. -Chem., A 7(8), 1677.

YAMAUCHI, J. and OKAMURA, T., Jpn. Pat. 72 19, 421 (1972); Chem. Abstr. 78, 17519) (1973).

YAMAUCHI, J. and OKAMURA, T., Jpn. Pat. 72 19, 422 (1972); Chem. Abstr. 78, 5345 m (1973)