Oligomeric Benzoin Photoinitiators

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ABSTRACT: Novel oligomeric photoinitiators were synthesised by reacting benzoin with isophorone diisocyanate-terminated oligomers of dihydroxy-terminated depolymerization products of polyethylene terephthalate (PET). PET was depolymerized by ethylene glycol (EG), hexylene glycol (HG), polyethylene glycol 10 000 (PEG), and α, ω-dihydroxy poly(dimethyl siloxane)s (PDMS). Oligomeric photoinitiators were used as free radical initiators for polymerization of styrene and acrylonitrile. Formation of block copolymers was illustrated by several characterisation methods such as FTIR, ^{1}H-NMR, DSC, and GPC. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 500–508, 2002

Key words: polystyrene; photopolymerization; copolymerization; polysiloxanes

INTRODUCTION

Recently, much interest has been shown in polymeric and oligomeric photoinitiators[1] that may have better compatibility, storage stability, and greater reactivity.[2] A number of polymer[1,2] and resin[3]-bound benzoin and benzoin ethers were described before. Polymer-bound photoinitiators were prepared by either copolymerization of vinyl monomer containing photoinitiator moiety or by linking the photoinitiator to polymer backbone. The main cleavage for polymer-bound benzoin photoinitiators was shown to be mainly α-cleavage. If secondary cleavage occurs, benzoin molecules is freed from the polymer backbone and initiation occurs by free radicals.[4] Polymer-bound benzoin methyl ester is four times more effective than benzoin methyl ester, and this may be due to the gel effect, which reduced the termination rate and their different reactivity of benzoin anchored to the polymeric matrix.[5]

To improve storage stability and compatibility of benzoin alkyl ether photoinitiators in UV-curable formulation, polymeric or oligomeric systems having benzoin alkyl ethers moieties as end groups have been designed.[6] They were prepared from diisocyanate ended poly(tetramethylene glycol). Furthermore, ketonic resin-bound benzoin and benzoin ether photoinitiators with higher reactivities than the corresponding benzoin/benzoin ether were produced *in situ* before by adding benzoin into the reaction mixture during resin preparation.[7]

In this work, oligomeric photoinitiators were synthesised from depolymerized PET[7] and used as initiators for polymerization of styrene and acrylonitrile to obtaine block copolymers.

EXPERIMENTAL

Materials

Depolymerization of PET was carried out as described earlier.[7] Isophorone diisocyanate (IPDI) was a product of Fluka AG (Buchs, Switzerland) and used without purification. Dibutyltin dilaurate (T12) catalyst was a product of Fluka AG.

Table I   Preparation Conditions and Characteristics of Oligomeric Photoinitiators

DITD PET	Isocyanate Weight (wt %)	M_n[a] (g/mol)	(y + 1)[b]
PET Si	2.4 ± 0.05	3500 ± 75	1
PET HG	11.05 ± 0.02	760 ± 2	1
PET PG	0.24 ± 0.01	35150 ± 1550	1.7
PET EG	4.7 ± 0.10	1785 ± 40	2.5

[a] Calculated from isocyanate content.
[b] Average number of terephthaloil groups per molecule calculated from M_n values.

Styrene (St) (from Petkim Petrochemical Company, Izmit, Turkey), was washed with 10% aqueous NaOH solution, dried over $CaCl_2$, and freshly distilled in a vacuum. Benzoin was a product of Fluka AG and used as received. Solvents used were products of Merck AG (Darmstadt, Germany).

Analyses

Polymerization yield is defined as follows:

$$\text{Yield (\%)} = \frac{\text{Copolymer (g)}}{\text{Initiator (g) + monomer (g)}} \times 100$$

Isocyanate and peroxygen analyses were performed by using standart method.[8,9] Infrared (IR) spectra were recorded on a JASCO FTIR-5300 Fourier transform infrared spectrometer. ^{1}H-NMR spectra of macroinitiator and copolymers were obtained for $CDCl_3$ and DMSO solution on a Bruker (250 MHz) spectrophotometer.

M_n and M_w values of block copolymers were calculated by the gel permation chromatographic (GPC) method according to standart polystyrene calibration using a Knauer M64 instrument, and tetrahydrofuran (THF) served as eluent at 25°C. The flow rate was 1 mL/min.

DSC thermograms were obtained by using a Perkin-Elmer DSC-6 Instrument; heating rate was about 10°C min^{-1} under nitrogen atmosphere.

Molecular weights of copolymers were determined by the viscometric method. Specific viscosities of copolymers containing polystyrene were also measured in toluene. The following viscosity–molecular weight relationships were used depending on the middle group of copolymers.[10,11]

$$[\eta] = 4.4 \times 10^{-5} M_n^{0.65} \quad \text{(at 25°C)}$$

(used for PEG containing samples)

Viscosities of copolymers containing a polyacrylonitrile solution in dimethyl formamide were measured at 25°C using a Canon-Fenske capillary viscometer, and molecular weights were calculated from single-point value by using the following equations.[12,13]

$$[\eta] = \frac{\eta_{sp}/c}{1 + 0.28 \times \eta_{sp}}$$

$$[\eta] = 2.33 \times 10^{-4} M_n^{0.75}$$

Preparetion of Oligomeric Photoinitiators (DIBTD PET)

In the first step PET was depolymerized by using diols such as ethylene glycol (EG), hexylene glycol (HG), polyethylene glycol 10,000 (PEG) and α,ω-dihydroxy poly(dimethyl siloxane)s (PDMS).

The depolymerization experiments were carried out in a Dean-Stark apparatus by glycolysis in the presence of titanium tetra isopropylate as a catalyst under nitrogen atmosphere at 205°C. These dihydroxy-terminated depolymerization products of polyethyleneterephthalate (DHTD PET) were reacted with isophorone diisocyanate (IPDI) at 60°C in dichloro ethane solution under a blanket of dry nitrogen for 80 h. The molar ratio of IPDI to DHTD PET was held at 3 to prevent chain extension. The products were isolated by precipitating in acetonitrile or petroleum ether and filtered. The isocyanate contents of the end-
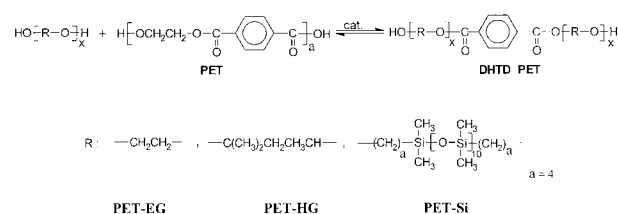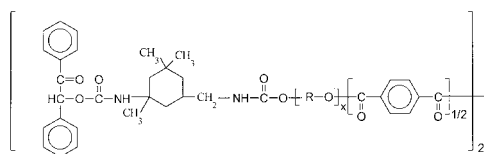

Scheme 1
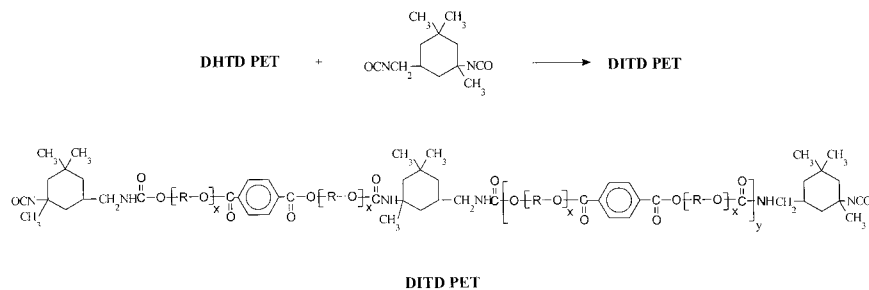
Scheme 2

capped products were determined by end-group titration of isocyanates. The calculated molecular weights are given in Table I. After the isolation, diisocyanate-terminated depolymerized polyethyleneterephthalate (DITD PET), were reacted with benzoin in methylene chloride by using dibutyltin dilaurate (T12). The reaction was carried out under nitrogen atmosphere at room temperature in dark for about 200 h. The resulting products (dibenzoin-terminated depolymerized polyethyleneterephthalate (DBTD PET)) were isolated by precipitating in petroleum ether or acetonitrile. Filtered products were dried in vacuum at room temperature, and used as photoinitiators for the polymerization of styrene and acrylonitrile. The structural formula of photoinitiators can be represented in the scheme 2 where *R* is as in the scheme I.

Photopolymerization

These oligomeric photoinitiators (DBTD PET) were used to prepare block copolymers of styrene and acrylonitrile. The procedures were as follows:

1. Oligomeric photoinitiator was dissolved in 2 mL of chloroform and 2 mL of styrene were placed in a Pyrex tube. The mixture was degassed in the usual manner prior to irradiation with an annular-type photoreactor equipped with lamps emitting at 350 nm at 25°C. After 3 h, the polymer was

precipated by pouring the mixture into methanol, then filtered, washed several times with petroleum ether, and dried in vacuum at 30°C for 24 h.
2. Oligomeric photoinitiator was dissolved in 2 mL of acrylonitrile were placed in Pyrex tube. The mixture was degassed, irradiated, and then recovered as described above.

RESULTS AND DISCUSSION

Results of photopolymerization of styrene and acrylonitrile with oligomeric photoinitiators are shown in Table I. Four type of oligomeric photoinitiator DBTD PET were prepared by using depolymerized PET with oligomeric diols, i.e; PET Si (by using PDMS), PET HG (by using hexylene glycol), PET PG (by using PEG), and PET EG (by using ethylene glycol). Table I contains the characteristic of photoinitiators in different preparation steps. The molecular weights of isocyanate-ended products (DITD PET) obtained in the first step of their preparation are higher than ex-
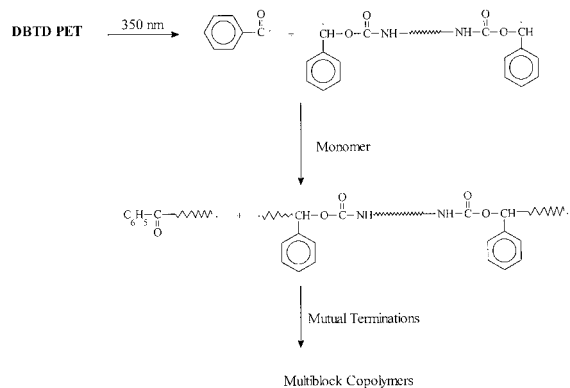

**DBTD PET**

Scheme 3

Scheme 4

Scheme 5

pected, probably due to some chain extention. This shows that PET PG and PET EG of DITD PET contain more than one trephthaloil group. These DIBTD PET were used as starting material for the synthesis of ABA-type styrene containing block copolymers.

ABA-type block copolymers of styrene and oligomeric middle blocks may be represented as follows (where R is as in the scheme I). Initiating of styrene is possible from both ends of the oligomeric initiators. Homopolystyrene produced by the benzoin radical may be terminated by growing chains of polystyrene produced by alkocyben-
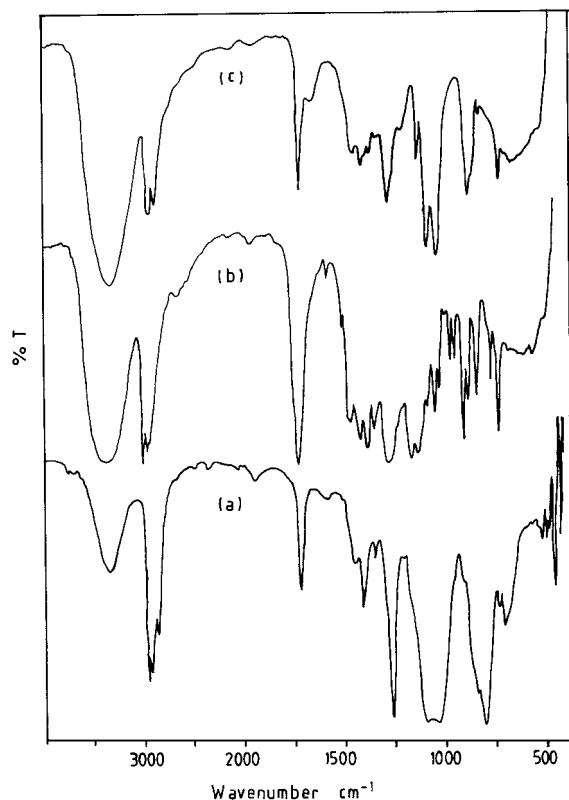

Figure 1 FTIR spectra of dihydroxy-terminated depolymerization products of polyethyleneterephthalate (DHTD PET) by using (a) α,ω-dihydroxy poly(dimethyl siloxane), (b) hexylene glycol, (c) ethylene glycol.
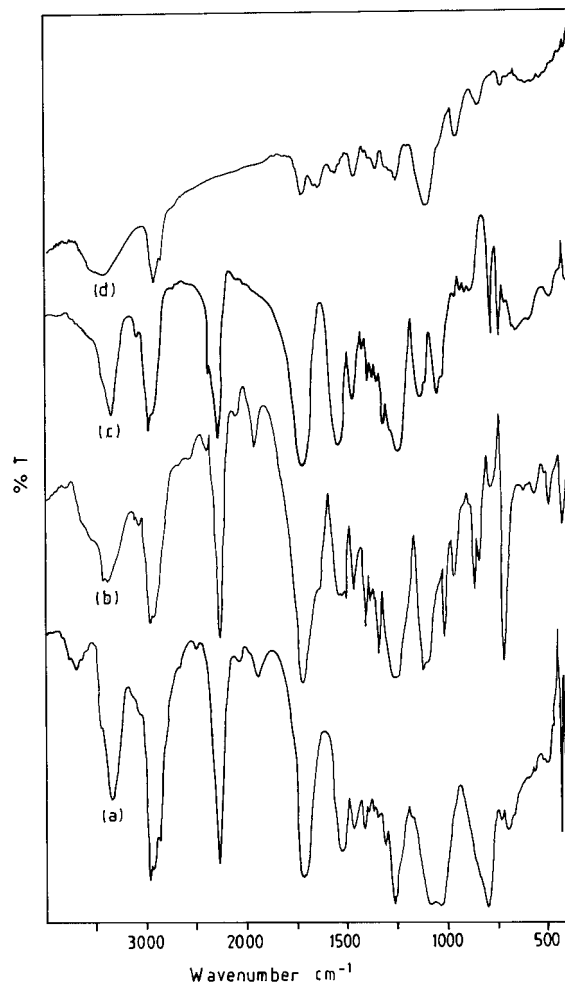
Figure 2 FTIR spectra of diisocyanate-terminated depolymerization products of polyethyleneterephthalate (DITD PET) by using (a) α,ω-dihydroxy poly(dimethyl siloxane), (b) hexylene glycol, (c) ethylene glycol, (d) poly(ethylene glycol) 10,000,

zyl radicals. This termination reaction reduces the amount of homopolymer.

Intermediates and the products were characterized by FTIR spectroscopy. In the FTIR spectra of DHTD PET products (Fig. 1) the peak at about 3350 cm^{-1} is due to —OH groups and at 1720 cm^{-1} is due to carbonyl groups. The peaks observed at between 1667 cm^{-1} to 2000 cm^{-1} are typical peaks p-substituted benzen compounds. In Figure 1 (a) the peaks appeared at 800 cm^{-1} and 1030 cm^{-1} are due to Si—CH$_3$ and Si—O bands, respectively. The —OH absorption peak at 3400 cm^{-1} dissappeared at the end of the capping reaction with isocyanate (Fig. 2). The peak at 2280 cm^{-1} is due to the stretching vibration of —NCO,
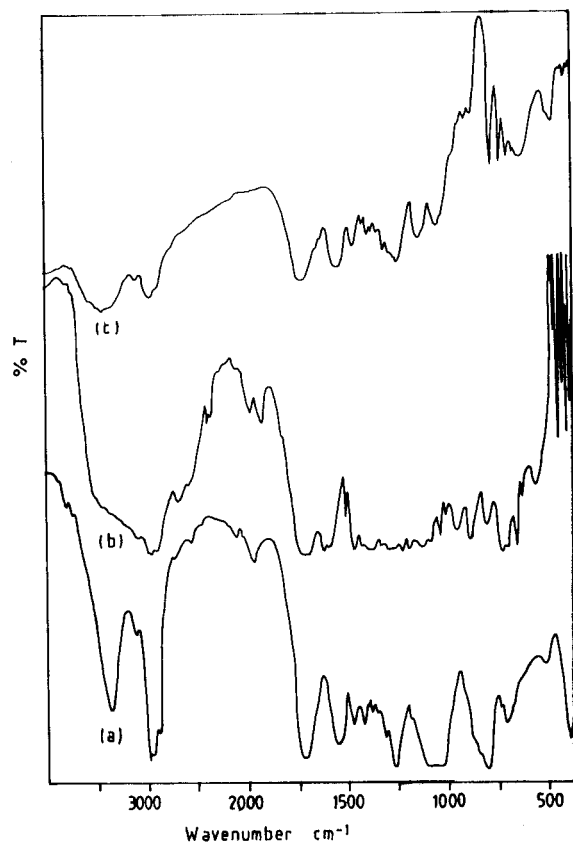
Figure 3 FTIR spectra of photoinitiators (a) PET Si–Benzoin, (b) PET HG–Benzoin, (c) PET EG–Benzoin.

and it is the principal absorption peak for isocyanate groups. The peaks observed at about 3440 cm^{-1} are due to —NH streching of urethane groups. The disappearence of the —NCO peaks indicates the formation of DBTD PET (Fig. 3). FTIR spectra of styrene copolymers are shown in Figure 4. The typical peaks of PS appeared in between 1667–2000 cm^{-1}, which are due to a monosubstituted benzene structure. The urethane peaks at about 3440 cm^{-1} are observed in all copolymers, which indicates the incorporation of DBTD PET into the copolymers. FTIR spectra of copolymers containing acrylonitrile (Cop. Nos. 2, 5, and 7) are presented in Figure 5. The typical peaks of PAN at 2250 cm^{-1} due to C≡N stretching vibration and the urethane peaks at about 3440 cm^{-1} are observed in these copolymers.

^{1}H-NMR spectrum of samples were used for structure determination and for molecular weight calculations. Observed signals due to corresponding nuclei are summarized in Table II. The signals at 0.8 and 2.5 ppm are due to the —CH$_2$ and

—CH protons of polystyrene blocks. The signals appered at 6.5 and 7.0 ppm are due to phenyl protons of polystyrene segments. The specific signals of —CH$_2$ protons of PEG blocks of copolymer No. 3, No. 4, No. 5, No. 6, No. 7 can clearly be seen at about 4 ppm.

Weights of the samples in the PET Si and PET PG series decrease with increasing DBDT PET weight percent in the copolymers.

The glass transition temperatures of the copolymers were determined by DSC (Table III). In these block copolymers three different special groups affect the thermal behavior of samples. Terephthaloil groups are in the middle, and PS chains in the outer. EG, HG, PEG, and PDMS groups are between these two hard segments. T_g values of copolymers are from PS segments that have much higher molecular weight than the photoinitiators segment. The glass transitions tem-
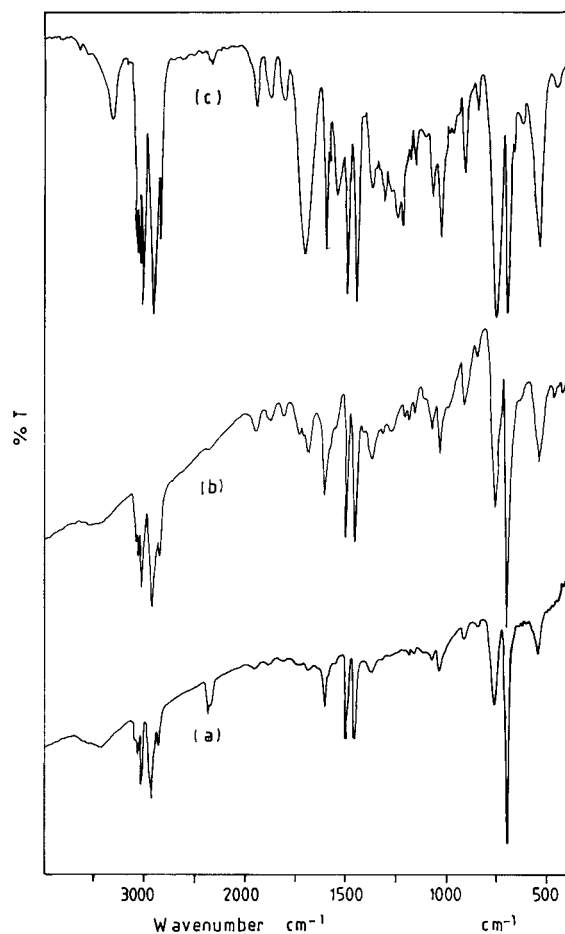
Figure 4 FTIR spectra of styrene copolymers (a) Cop. No. 4, (b) Cop. No. 3, (c) Cop. No. 6.
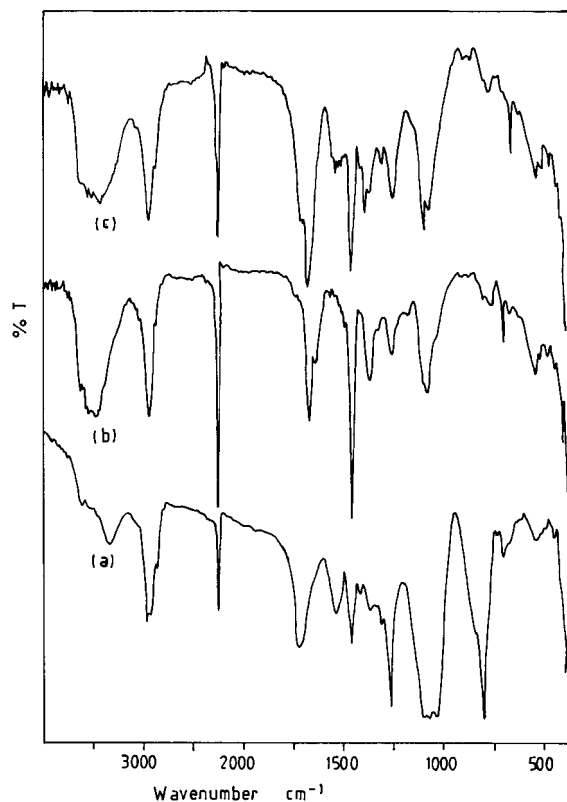
Figure 5 FTIR spectra of acrylonitrile copolymers (a) Cop. No. 2, (b) Cop. No. 5, (c) Cop. No. 7.

perature of PET Si-containing block copolymers (Cop. No. 1) is not observed. Besides, the glass transitions temperature of block copolymers (Cop. Nos. 3, 4, 6) are similar to polystyrene homopoly-

mer, and the glass transitions temperature of block copolymers (Cop. Nos. 2, 5, 7) slightly lower than T_g of PAN. Melting temperature (T_m) of copolymers (Cop. Nos. 6 and 7) are due to the DBTD PET EG segment that have T_m value of 109.5°C.

Intrinsic viscosities and molecular weights of copolymers containing polyacrylonitrile or polystyrene were calculated from appropriate equations (Table III).

The composition of copolymers calculated by NMR and initial mol ratio of monomer to initiator are shown in Table IV. Comparable results were obtained suggesting that nearly all of the initiator molecules were included in the copolymers by considering their high molecular weights. The structure of copolymers should be multiblock type as shown below. Calculated n and m values are shown in Table IV. Some homopolymers present in the copolymers may slightly effect these calculated values.

CONCLUSION

In this work, PET was depolymerized with a thermal treatment method by using α,ω-dihydroxy poly (dimethyl siloxane), hexylene glycol, poly-(ethylene glycol) 10,000, and ethylene glycol. Oligomeric photoinitiators containing benzoin were synthesized from these depolymerized products and used as initiators for polymerization of styrene and acrylonitrile to obtain ABA-type block copolymers and multiblock copolymers. These co-

Table II ^{1}H NMR Spectral Data of the Copolymers and DBTD PET δ ppm

Sample No.	—CH$_3$	—CH, —CH$_2$—	Aromatic —CH	(CH$_3$)$_2$Si—O	—Si—CH$_2$—	—NH—CH$_2$—	—CH$_2$—O—
DBTD PET Si	1.1	0.8–2.2	6.8–8.1	0.043 0.05–0.1	0.6	2.2	4
DBTD PET EG	1.1	0.8–1.8	6.1 6.8–8.1	—	—	2.5	4.2
Cop. No 2	1.1	0.9–1.8 2.1–3.5	7.2–7.8 8.1–8.2	0.043 0.05–0.1	0.6	2.3	3.8
Cop. No 3	1.1	0.8–2	6.4–7.2 8.2	—	—	2.3	4
Cop. No 4	1.1	0.8–2.2	6.3–7.2 8	—	—	2.2	4
Cop. No 5	1.1	1.8–2.5 3.7	6.8–7.2 7.6	—	—	2.3	4
Cop. No 6	1.05	1–1.8	6.4–7.2 7.7	—	—	2.2	4.2
Cop. No 7	1.1	0.8–1 3.15, 2.8	7.3, 7.9, 8.08	—	—	2.5	4.07

Table III   Conditions of Preparation and Some Characteristics of Block Copolymers

Block Copolymer No.	DBTD PET Type	Initial Composition		Yield (%)	$[\eta]$ (dL/g)	$M_v \times 10^{-3}$ (g/mol)	$M_n \times 10^{-3}$ (g/mol)[a]	$M_w \times 10^{-3}$ (g/mol)[a]	T_g (°C)	T_m (°C)	Acrylonitrile (w %)
		DBTD PET (w %)	Styrene (w %)								
—	DBTD PET EG	100	—		—	—					109.5
1	DBTD PET Si	15	85	—	75	—	—			—	—
2	DBTD PET Si	15	—	85	100	2.58	247	—	—	80	
3	DBTD PET HG	5	95		80	0.32	87	50	99	94	—
4	DBTD PET PG	15	85	—	88	0.10	158	75	174	96	—
5	DBTD PET PG	5	—	95	100	2.21	200	—	—	75	—
6	DBTD PET EG	15	85	—	85	0.54	490	474	524	98	63
7	DBTD PET EG	10	—	90	100	1.64	135	—	—	80	62.5

[a]Obtained from GPC.

Table IV The Composition of Copolymer

| Block Copolymer No. | Initiator | Mol Weight[a] of Initiator | Initial Composition | | | Copolymer | | | |
			Initiator mol	Styrene mol	Acrylonitrile mol	Mol Ratio of Initiator/Monomer	Mol Ratio from Initiator/Monomer	m	n
1	DBTD PET Si	3920 ± 75	0,0042	0,82	—	1:195	—	—	—
2	DBTD PET Si	3920 ± 75	0,0042	—	1,6	1:380	1:400	400	10
3	DBTD PET HG	1182	0,0066	0,91	—	1:137	1:137	137	5.6
4	DBTD PET PG	35570	0,00042	0,82	—	1:1952	1:3300	500	1
5	DBTD PET PG	35570	0,00014	—	1,8	1:12857	—	—	—
6	DBTD PET EG	2205	0,0084	0,82	—	1:98	—	98	40
7	DBTD PET EG	2205	0,0056	—	1,7	1:303	1:200	200	10

[a] Calculated from Table I.

polymers showed appreciably different properties than their homopolymers.

The terephthaloil group in the middle of polymer chain effects the thermal and mechanical characteristics of block copolymers. Copolymers have lower T_g values than corresponding homopolymers of styrene and acrylonitrile.

This novel photoinitiating system may be used to prepare multiblock copolymers of vinyl monomers with a variety of condensation-type oligomers. Besides, in UV curing technology, they may be used for photoinitiation.

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