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Negative-type soluble photosensitive polyimides derived from benzhydroltetracarboxylic dianhydride: synthesis and characterization

G. Rames-Langlade*, P. Monjol and H. Sekiguchi
Laboratoire de Chimie Macromoléculaire, URA 024, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

and R. Mercier, and B. Sillion
LMOPS (Laboratoire des Matériaux Organiques à Propriétés Spécifiques), BP no. 4, 69390 Vernaison, France

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The present paper deals with the synthesis and the characterization of negative-type soluble photosensitive polyimides based on benzhydroltetracarboxylic dianhydride. These polymers were prepared either by a thermal or chemical imidization, and the photoreactive methacryloyl group was introduced through the reaction between the hydroxyl group and the isocyanate group of methacryloyl isocyanate to yield a carbamate linkage. Bis(4-aminophenyl)methane, bis(3,5-dimethyl-4-aminophenyl)methane and bis(3-methyl-5-isopropyl-4-aminophenyl)methane were used as aromatic diamines, and 1,1,1,3,3,3-hexafluoropropane-2,2-di(4′-phthalic anhydride) as aromatic dianhydride. 4-*N*,*N*-Dimethylamino-3′,5′-diaminobenzophenone was also used in order to produce an autophotosensitive polymer. The resulting methacryloyl carbamate-modified polyimides were found to be soluble in polar solvents and they were characterized by infrared and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopies. Inherent viscosities, glass transition temperatures, thermal behaviour and dielectric constants were also determined. © 1997 Elsevier Science Ltd.

(Keywords: imide formation; benzhydrol polyimide; photosensitive polyimide)

INTRODUCTION

It is well known that polyimides are useful to the electronics industry, e.g. as an insulator which retains its electrical and mechanical characteristics at relatively high temperature. However, conventional polyimides are not soluble in the imidized form. So, their solvent-soluble precursor form has been used during the past two decades for polyimide layer direct patterning processes. The photosensitive group (generally methacrylate or acrylate) is attached to the carboxyl group of the polyamic acid through either an ester linkage[1–3] or in the form of a tertiary amine salt[4]. However, this kind of polymer has a limited shelf-life stability, and the curing of photosensitive polyimide precursors required for the conversion into polyimides causes the release of volatiles such as residual solvents, alcohols or water (depending on the precursor type) and photoreacted groups. Hence, photostructures shrink (about 50%), images are distorted, and stresses are induced. Therefore, in order to eliminate these drawbacks the synthesis of fully imidized solvent-soluble photosensitive polyimides has been undertaken. They should be the ideal candidates on account of their storage stability, their lower shrinkage (<20%) and because they do not require curing temperatures as high as those for precursors. Nowadays, there are a wide variety of soluble, thermally stable polyimides in which solubility is provided either by the introduction of flexible thermally stable links (such as isopropylidene, perfluoro isopropylidene, ether or carbonyl) or bulky side groups in the backbone or by the disruption of regularity through the copolymerization of two dianhydrides or two diamines[5]. However, until now few examples of fully imidized solvent-soluble photosensitive polyimides have been reported in the literature. They may be obtained by incorporating a photoreactive group into a soluble polyimide. Lee and Lee[6] made a photoreactive polyimide prepared from diaminobenzoic acid as comonomer in which the free carboxylic acid is converted into methacrylic acid glycidyl ester. Nishizawa *et al.*[7] described the modification of phenolic groups from the diamine unit by the reaction with methacryloyl ethyl isocyanate. They may also be obtained by the condensation of aromatic dianhydride with aromatic diamine substituted for photoreactive groups such as acrylamide[8] or ethyl methacrylate[9]. A soluble autophotosensitive polyimide (negative-type) based on benzophenone and thioxanthone chromophores which are able to initiate the photochemical reaction, was also reported by Rohde *et al.*[10].

Malinge *et al.*[11] have developed a new approach to obtain soluble imidized structures by the condensation of

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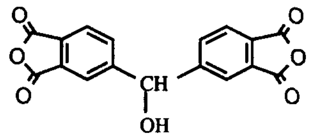
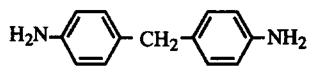
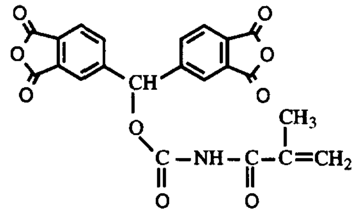
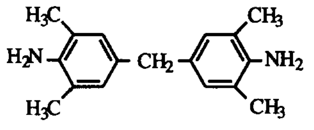
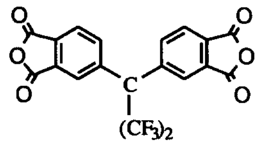
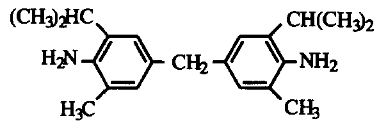
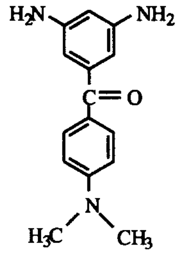
* To whom correspondence should be addressed

Table 1 Aromatic dianhydrides and diamines used for the preparation of photosensitive polyimides

Aromatic dianhydride	Aromatic diamine
 BHTDA	 MDA
 BHTDA*	 MDA4Me
 6FDA	 MIPA
	 MKDA

benzhydroltetracarboxylic dianhydride (BHTDA) with aromatic diamines. The presence of a benzhydrol unit in the main chain is suitable for preparing a polyimide soluble in organic solvents and, moreover, the alcohol function allows the incorporation of a photosensitive group. Berrada *et al.* have recently[12] described the preparation of new solvent-soluble fully imidized photosensitive homopolyimides from BHTDA. The photosensitive functional groups were incorporated through the reaction between the alcohol group of BHTDA and photoreactive acid groups using dicyclohexylcarbodiimide with dimethylaminopyridine as a catalyst. These BHTDA esters were then polycondensed with aromatic diamines and imidized chemically to obtain the corresponding polyimide esters. This method avoids contamination of the BHTDA derivatives by ionic impurities such as chlorine. However, they have noticed a difficulty in removing the dicyclohexylurea impurities formed during the reaction. These results led us to choose methacryloyl isocyanate (MAI)[13], as the acylating reagent. MAI exhibits the following advantages: the reaction between the isocyanate function and hydroxyl group is very fast without requiring a catalyst or producing secondary products, and the resulting methacryloyl carbamate structure is highly photoreactive and small enough for the decomposition of the cross-linker.

In this paper, the synthesis and the characterization of a series of negative-type soluble photosensitive polyimides based on BHTDA and MAI are described. The synthesis was carried out by the classical method via amic acid of which the cyclodehydration was realized either by heat or by using chemical reagents. By both these methods, photosensitive homopolymers and copolymers were prepared successfully. Bis(4-aminophenyl)methane (MDA), alkyl substituted diamines such as bis(3,5-dimethyl-4-aminophenyl)methane (MDA4Me) and bis(3-methyl-5-isopropyl-4-aminophenyl)methane (MIPA), and a fluorinated dianhydride such as 1,1,1,3,3,3-hexafluoropropane-2,2-di(4-'phthalic anhydride) (6FDA) (*Table 1*) were used. An aromatic diamine, 4-*N*,*N*-dimethylamino-3',5'-diaminobenzophenone (MKDA) (*Table 1*) was also incorporated into the polymer backbone in order to obtain an autophotosensitive polyimide. Since these photosensitive polyimides would be used as negative-type photoresists for microelectronic applications, the purpose of this work will be to investigate further the effect caused by the imidization method used and by the introduction of comonomers on the photocrosslinkage ability.

EXPERIMENTAL

Measurements

Infrared (i.r.) spectra were recorded on powder (KBr pellet) using a Bruker Fourier transform infra-red (*FT*i.r.) IFS 45 spectrophotometer. Proton and carbon nuclear magnetic resonance (n.m.r.) spectra were recorded with either a Bruker ACE 200, AM 250 or AC 300 spectrometer operating at nominal frequencies of 200, 250 and 300 MHz for ^{1}H and ^{13}C. The inherent viscosity of polyimide in *N*-methylpyrrolidone (NMP) ($C = 1\ \mathrm{g\ dl^{-1}}$) was measured at 25°C with a Ubbelohde viscometer. Thermal studies were evaluated by using a Du Pont Instrument 910 for differential scanning calorimetry (d.s.c.) and a Du Pont Instrument 951 for thermogravimetric analysis (t.g.a.): d.s.c. and t.g.a. were carried out under a nitrogen atmosphere with $10^\circ\mathrm{C\ min^{-1}}$ temperature ramps. Dielectric constants were determined by using an Analyser 2970 TA instrument with temperature and frequency ranges from 30 to 350°C and from 1 to 200 kHz, respectively, with sputter sensors coated. These measurements were performed on polyimide films prepared in NMP and dried for several hours *in vacuo* at 100°C.

Materials

MDA (Merck) was purified by recrystallization from a mixture of water and methanol. MDA4ME (Aldrich Chemical Co.) was recrystallized from methanol. MIPA (Lonza Chemical) was recrystallized from cyclohexanol. The MKDA was kindly provided by Cemota and was used as received. The BHTDA was prepared according to the method reported by Malinge *et al.*[11] and was further purified by a lyophilization in dioxane, then by washing with pentane. Methyne-bis-phenyl-3,4,3′,4′-tetracarboxylic dianhydride-(3)-methacryloylcarbamate (BHTDA*) was synthesized according to the method previously reported[14]. The 6FDA (American Hoechst Co.) was refluxed in acetic anhydride for 2 h, filtered, and then dried at 150°C for 3 h prior to use. MAI, kindly provided by Nippon Paint, was divided into several small aliquots stored at −18°C and sheltered from light. It was used without further purification. NMP was distilled over calcium hydride under nitrogen. *meta*-Cresol was distilled twice under reduced pressure. Triethylamine and propionic anhydride were distilled rapidly.

General procedure for preparation of photosensitive methacryloyl carbamate-modified polyimides by thermal imidization (**1a***, **1b***, **2***, **3*** *and* **4***)

The synthesis of **1a*** is given as a typical synthetic example. A 100 ml four-necked round-bottom flask fitted with a mechanical stirrer, nitrogen gas inlet and glass funnel was scrupulously dried. The apparatus was charged with 8 g of BHTDA (2.47 mmol), and 20 ml of *m*-cresol was added via syringe (under nitrogen) while stirring MDA (4.89 g) (2.47 mmol), dissolved in 30 ml of *m*-cresol (20% w/w), was rapidly added to the dianhydride solution. The reaction mixture became soluble and the solution was stirred at room temperature overnight in nitrogen to provide polyamic acid. The glass funnel was then replaced by a reflux condenser and the reaction flask was heated to 120°C for 30 min, then to 180°C for 3 h. The solution was cooled slightly, diluted with 50 ml of *m*-cresol, then poured into about 1 l of methanol. The powder was washed several times with fresh methanol and dried at 150°C for 24 h *in vacuo* to give 11.52 g of **1** (95%).

1. ^{1}H n.m.r. (DMSO-d_6, ppm): 4.2 (*s*, 2H), 6.25 (*s*, 1H), 6.72 (*s*, 1H), 7.4 (*s*, 8H), 8 (*dd*, 4H), 8.1 (*s*, 2H).
^{13}C n.m.r. (DMSO-d_6, ppm): 73.2, 121.1, 123.9, 127.1, 129.1, 130, 130.7, 131.1, 131.4, 140.7, 152.1, 166.4, 167.

2. ^{1}H n.m.r. (DMSO-d_6, ppm): 2.0 (*s*, 12H), 3.8 (*s*, 2H), 6.25 (*s*, 1H), 6.72 (*s*, 1H), 7.2 (*s*, 4H), 8 (*dd*, 4H), 8.1 (*s*, 2H).
^{13}C n.m.r. (DMSO-d_6, ppm): 17.4, 73.2, 121.1, 123.8, 127.1, 128.5, 130.3, 131.8, 132.6, 136.6, 141.8, 152, 166.4, 166.7.

3. ^{1}H n.m.r. (DMSO-d_6, ppm): 2.0 (*s*, 6H), 3.8 (*s*, 1H), 4.2 (*s*, 1H), 6.24 (*s*, 1H), 6.72 (*s*, 1H), 7.14 (*s*, 2H), 7.3 (*m*, 4H), 8 (*m*, 6H).
^{13}C n.m.r. (DMSO-d_6, ppm): 17.4, 73.2, 120.8, 121.2, 123.5, 123.8, 127.2, 127.9, 128.4, 129, 129.9, 130.2, 130.4, 131.6, 131.8, 132.2, 132.5, 136.5, 140.7, 141.7, 151.5, 151.6, 151.8, 152.1, 166.4, 166.6, 166.7.

4. ^{1}H n.m.r. (DMSO-d_6, ppm): 4.2 (*s*, 2H), 6.25 (*s*, 0.6H), 6.72 (*s*, 0.6H), 7.4 (*s*, 8H), 7.9–8.22 (*m*, 6H).
^{13}C n.m.r. (DMSO-d_6, ppm): 74.5, 121.6, 124.5, 125, 127.7, 129.8, 130.4, 130.8, 131.2, 132.9, 133.3, 133.7, 136.5, 138, 141.2, 142, 152.5, 166, 166.1, 166.7, 166.8.

The chemical modification of the above polymer by reaction with MAI is carried out as follows: first, 2 g of **1** (4.11 mmol) placed in a 100 ml three-neck round-bottom flask was dissolved with 18 ml of NMP, then 0.6 ml of MAI (5.78 mmol) was then added dropwise to the polymer solution and stirred overnight at room temperature. The resulting polyimide methacryloyl carbamate (**1a***) was diluted with NMP, poured into water, washed with methanol and dried at 50°C for 16 h *in vacuo*.

1a*. ^{1}H n.m.r. (DMSO-d_6, ppm): 1.9 (*s*, 3H), 4.2 (*s*, 2H), 5.7–5.9 (*d*, 2H), 7.3 (*s*, 1H), 7.38 (*s*, 8H), 8.0–8.22 (*m*, 6H), 10.9 (*s* 1H).
^{13}C n.m.r. (DMSO-d_6, ppm): 18, 75.6, 121.1, 123.2, 123.9, 127.3, 129, 129.8, 131.5, 132.5, 138.7, 141.2, 146.6, 150.2, 166.5.

1b*. ^{1}H n.m.r. (DMSO-d_6, ppm): 1.9 (*s*, 1.8H), 4.2 (*s*, 2H), 5.7–5.9 (*d*, 1.2H), 6.25 (*s*, 0.4H), 6.7 (*s*, 0.4H), 7.3 (*s*, 0.6H), 7.38 (*s*, 8H), 8.0–8.22 (*m*, 6H), 10.9 (*s*, 0.6H).

2*. ^{1}H n.m.r. (DMSO-d_6, ppm): 1.9 (*s*, 3H), 2.0 (*s*, 12H), 3.8 (*s*, 2H), 5.7–5.9 (*d*, 2H), 7.1 (*s*, 4H), 7.35 (*s*, 1H), 8.1–8.2 (*dd*, 4H), 8.3 (*s*, 2H), 10.9 (*s*, 1H).

3*. ^{1}H n.m.r. (DMSO-d_6, ppm): 1.9 (*s*, 3H), 2.0 (*s*, 6H), 3.8 (*s*, 1H), 4.2 (*s*, 1H), 5.7–5.9 (*d*, 2H), 7.18 (*s*, 2H), 7.22 (*s*, 1H), 7.3 (*m*, 4H), 8.1–8.25 (*m*, 6H), 10.9 (*s*, 1H).

4*. ^{1}H n.m.r. (DMSO-d_6, ppm): 1.9 (*s*, 1.8H), 4.2 (*s*, 2H), 5.7–5.9 (*d*, 1.2H), 7.3 (*s*, 0.6H), 7.4 (*s*, 8H), 7.9–8.22 (*m*, 6H), 10.9 (*s*, 0.6H).

General procedure for the preparation of photosensitive methacryloyl carbamate-modified polyimides by chemical imidization (**5***, **6***, **7*** *and* **8***)

The synthesis of **5*** is given as a typical synthetic example. In the same apparatus as described above, 3.48 g of BHTDA* (8.00 mmol) and 10 ml of NMP were introduced. MDA (1.58 g) (8.00 mmol) dissolved in 10 ml of NMP (20% w/w) was rapidly added under stirring, then stirring was kept on at room temperature overnight in nitrogen. The resulting polyamic acid solution was diluted with 10 ml of NMP and then 12 ml of propionic anhydride (93.60 mmol) and 7 ml of triethylamine (50.22 mmol) were added. The mixture was stirred at 25°C overnight, in nitrogen. The resulting polymer (**5***) solution was diluted with 50 ml of NMP, poured into 1.5 l of water, washed several times with methanol and then dried at 50°C for 24 h *in vacuo* to give 3.7 g of **5*** (95%).

5*. ^{1}H n.m.r. (DMSO-d$_6$, ppm): 1.9 (*s*, 3H), 4.1 (*s*, 2H), 5.7–5.9 (*d*, 2H), 7.3 (*s*, 9H), 8.0–8.22 (*m*, 6H), 10.9 (*s*, 1H).

6*. ^{1}H n.m.r. (DMSO-d$_6$, ppm): 1.9 (*s*, 3H), 2 (*s*, 6H), 3.9 (*s*, 1H), 4.2 (*s*, 1H), 5.7–5.9 (d, 2H), 7.1 (*s*, 2H), 7.23 (*s*, 1H), 7.38 (*s*, 4H), 8.0–8.22 (*m*, 6H), 10.9 (*s*, 1H).
^{13}C n.m.r. (DMSO-d$_6$, ppm): 17.4, 17.8, 40. 76, 121, 121.4, 122.5, 123.5, 124, 127, 127.8, 128.2, 129, 130, 131, 131.2, 132, 132.3, 132.6, 132.8, 136.4, 138.9, 140.5, 141.5, 146.2, 146.5, 149.9, 165.8, 165.86, 166, 2, 166.7.

7*. ^{1}H n.m.r. (DMSO-d$_6$, ppm): 1.0 (*s*, 6H), 1.9 (*s*, 3H), 2.0 (*s*, 3H), 3.9 (*s*, 1H), 4.2 (*s*, 1H), 5.7–5.9 (*d*, 2H), 7.08 (*s*, 1H), 7.2–7.4 (*m*, 6H), 7.9–8.25 (*m*, 6H), 10.9 (*s*, 1H).
^{13}C n.m.r. (DMSO-d$_6$, ppm): 17.8, 18.3, 23.6, 28.2, 75.8, 121.2, 122, 123.7, 124.3, 124.7, 125, 126.5, 127.8, 128.5, 129.4, 130. 131.2, 131.6, 132.2, 132.8, 133.1, 136.6, 139, 141.3, 142.8, 146.8, 147, 147.1, 147.2. 147.5, 150.4, 166.66, 166.7, 166.8, 167.2.

8*. ^{1}H n.m.r. (DMSO-d$_6$, ppm): 1.9 (*s*, 3H), 3 (*s*, 0.6H), 4.1 (*s*, 1.8H), 5.7–5.9 (*d*, 2H), 6.8 (*s*, 0.3H), 7.22 (*s*, 1H), 7.3 (*s*, 0.72H), 7.9 (*d*, 0.4H), 8.0–8.2 (*m*, 6H), 10.9 (*s*, 1H).
^{13}C n.m.r. (DMSO-d$_6$, ppm): 17.4, 75.6, 111, 121, 122.5, 123, 124, 125, 127.8, 130, 131.8, 132.5, 132.6, 137.7, 139.5, 141.8, 146.5, 150, 153, 166.4, 166.55, 166.65, 166.8, 191.3

RESULTS AND DISCUSSION

Polymer synthesis

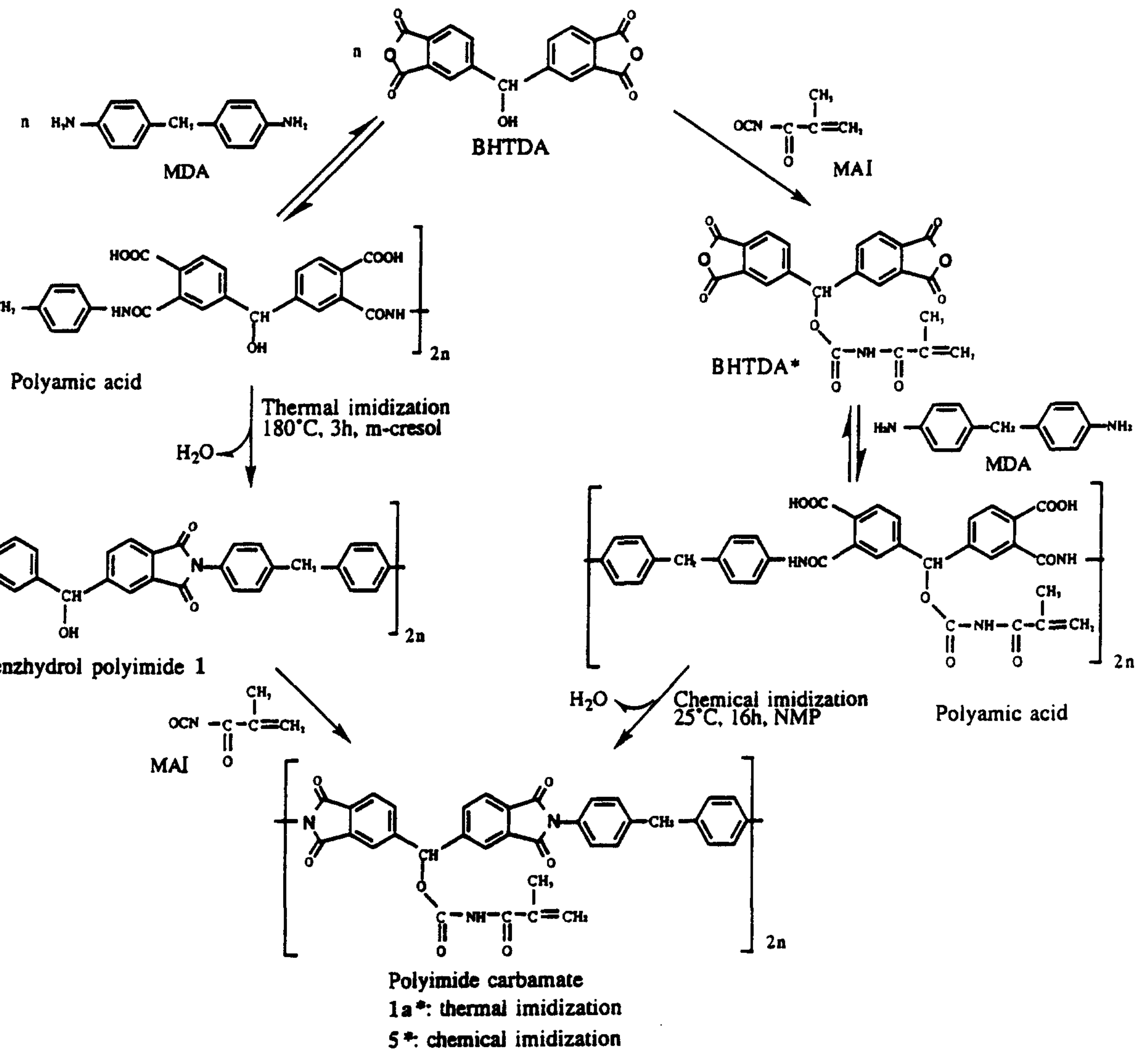
Reaction paths. The synthesis of soluble polyimides, carrying a photoreactive pendant group, from an aromatic dianhydride and an aromatic diamine, includes two different reactions: the formation of imide structures from dianhydride and the introduction of a photoreactive substituent from the hydroxyl group. The former reaction is carried out by the classical method, e.g. formation of polyamic acid followed by its cyclization into an imide group realized either by heat or chemical reagents. The latter reaction occurs between hydroxyl groups, either from BHTDA or from benzhydrol polyimide, depending on the method of cyclization used, and MAI. As an example, the reaction scheme of **1a*** and **5*** is outlined in *Scheme 1*. In the case of thermal imidization, because of the ease of thermal polymerization of the methacrylic double bond, a polymer from BHTDA and aromatic diamine is first prepared. The resulting benzhydrol polyimide is then made photosensitive by a reaction between its hydroxyl groups and MAI. The situation is different for the chemical imidization because the use of dehydrating agents to imidize would cause a partial esterification of the hydroxyl group. Therefore, BHTDA is first converted into the corresponding photosensitive dianhydride (BHTDA*) by reaction with MAI. The absence of methacrylic oligomers in BHTDA* is checked by gel permeation chromatography, and BHTDA* is then polycondensed with an aromatic dianhydride by using dehydrating agents at room temperature. The conditions of thermal and chemical imidization reactions have already been determined from methacryloyl carbamate bisimide model compounds and reported in a previous paper[14]. The thermal imidization is complete in 3 h at 180°C, whereas the chemical imidization requires 16 h at 25°C in the presence of propionic anhydride with triethylamine. In order to obtain high molecular weight chains[15], experimental precautions were taken during the polycondensation step: water was strictly removed from solvents, monomers and apparatus to avoid the hydrolysis of carbonyl functions from dianhydride and from polyamic acid. Strictly equimolar quantities of dianhydride and diamine were used. The chemical cyclodehydration was carried out with a mixture of propionic anhydride/triethylamine at a 2/1 molar ratio in order to avoid the degradation of the polyamic acid chain.

Choice of the imidization methods. The polycondensation of an aromatic dianhydride and an aromatic diamine, the method employed in the synthesis of polyimides, is a two-stage reaction leading first to polyamic acid and then to polyimide through a cyclodehydration reaction. The first step is crucial to attain high molecular weight chains, and the second one has a great influence on the final nature of the polyimide since a quantitative conversion in the cyclodehydration process is necessary to obtain a pure, wholly cyclized polyimide. This cyclization reaction is carried out either by thermal or chemical means. The amic acid–imide conversion attains its maximum during the thermal cyclization. However, it is accompanied by secondary reactions[16], producing branching in the polymer. Moreover, the amic acid–imide conversion is a reversible reaction, which means that, at high temperature, it releases water which is able to hydrolyse the amic acid group and therefore to reduce the molecular weight of the polymers. In the method using dehydrating agents, water is consumed by these reagents and becomes inactive. The chemical cyclization leads to linear and high molecular weight polymer, but the ratio of conversion of amic acid into imide units is lower than that obtained by thermal cyclization[15].

Choice of monomers. Attempts were made to obtain photosensitive polyimides having different chemical structures. A series of copolymers based on BHTDA (or BHTDA*) and MDA were synthesized by using either an alkyl substituted diamine in the *ortho* position, such as MDA4Me and MIPA, or a monomer carrying a perfluoromethyl group such as 6FDA. Certain homopolymers based on BHTDA (or BHTDA*) were synthesized with either MDA or MDA4Me. Attempts to obtain an autophotosensitive polyimide through the introduction into the backbone polymer of a functional group, which should be able to initiate the photopolymerization, was envisaged. In a previous investigation[14], we showed that the rate of photopolymerization and the degree of conversion of the methacryloyl double bond are the highest in the presence of Michler's ketone as a photoinitiator. Therefore, MKDA, which shows a structure close to that of Michler's ketone, could be an effective monomer for preparing an autophotosensitive polyimide.

Polymer characterization

Composition. The different polymers synthesized by a thermal and a chemical imidization are summarized in *Tables 2* and *3*, respectively. In the case of the thermal imidization method, benzhydrol polyimides (**1**, **2**, **3** and **4**) were first synthesized and the alcohol functions were then substituted by photoreactive methacryloyl groups with MAI to give the methacryloyl



Scheme 1 Two synthetic paths to polyimide carbamate

Table 2 Polymers synthesized by a thermal imidization

Dianhydride	Diamine	Benzhydrol polyimide	Polyimide carbamate	Degree of substitution[a] (%)
BHTDA	MDA	1	1a*	100
			1b*	60
BHTDA	MDA4Me	2	2*	100
BHTDA	MDA/MDA4Me (1/1)	3	3*	100
BHTDA/6FDA (3/2)	MDA	4	4*	60

[a] Calculated by ^{1}H n.m.r.

Table 3 Polymers synthesized by a chemical imidization

Dianhydride	Diamine	Polyimide carbamate
BHTDA*	MDA	5*
BHTDA*	MDA/MDA4Me (1/1)	6*
BHTDA*	MDA/MIPA (1/1)	7*
BHTDA*	MDA/MKDA (9/1)	8*

carbamate-modified polyimide (**1a***, **1b***, **2***, **3*** and **4***). Therefore, this method produces photosensitive polyimides with different degrees of substitution. However, due to the high reactivity of MAI, which induces the formation of impurities in MAI such as oligomers (but which do not react with alcohol functions), it is not possible to control the degree of substitution, and an excess of MAI was used for the modification of the hydroxyl group. By this method, complete substitution (**1a***, **2*** and **3***) and partial substitution (**1b***) were achieved. The benzhydrol copolyimide **4** contains 60 mol % of

Table 4 Yields, T_g values and viscosities of polyimides

Benzhydrol polyimide	Yield (%)	Tg (°C)	$[\eta]^a$ (dl g^{-1})	Polyimide carbamate	Yield (%)	$[\eta]^a$ (dl g^{-1})
1	96	270	0.58	**1a***		0.47
				1b*		0.51
2	94	210	0.63	**2***		0.80
3	95	210	0.56	**3***		0.66
4	91	286	0.41	**4***		0.43
				5*	95	0.88
				6*	94	0.45
				7*	93	0.92
				8*	96	1.00

^{a} Determined in NMP ($C = 1\,\mathrm{g\,dl^{-1}}$) at 25°C

the benzhydrol unit and the complete modification leads to a copolymer with 60% degree of substitution (**4***). In the case of the chemical imidization method, the methacryloyl carbamate-modified polyimides were obtained from BHTDA* and the polycondensation leads directly to a wholly substituted photosensitive polyimide. The homopolyimide **5*** and two copolyimides, one with 50 mol% of MDA4Me (**6***) and the other with 50 mol % of MIPA (**7***), were prepared. In the autophotosensitive polyimide (**8***), 10 mol % (4.5 wt%) of MKDA, which is the usual amount of photoinitiator generally necessary for the photopolymerization, was introduced.

Yield. The yields of polycondensation are higher than 90% (*Table 4*).

Viscosity. The resulting polymers have been found to be soluble in *N*-alkyl substituted amides. The inherent viscosities of benzhydrol polyimides and of methacryloyl carbamate-modified polyimides were measured at a concentration of 1 g dl^{-1} in NMP at 25°C. They were found to be in the range 0.4–1.0 dl g^{-1} (*Table 4*). In general, polyimides cyclized by the chemical method exhibit higher inherent viscosities than those cyclized by the thermal method.

Infrared. The *FT*i.r. analysis of benzhydrol polyimide and methacryloyl carbamate-modified polyimide was performed. The complete imidization was confirmed by the presence of characteristic imide absorption bands around 1780 and 1725 cm^{-1} and by the absence of amide carbonyl band located usually around 1690 cm^{-1}. The substitution of the hydroxyl group by a methacryloyl carbamate group was confirmed by the characteristic absorption at 990 cm^{-1} of the methacrylic double bond.

^{1}H and ^{13}C n.m.r. The ^{1}H n.m.r. spectroscopy determines the composition of the resulting polymers and estimates the degree of substitution for polyimides prepared by the thermal imidization. The composition of the copolymer was measured by the integration values of the signal due to the proton of methylene groups from the MDA unit (4.20 pm) and compared with that from the MDA4Me unit (3.8 ppm) for **3*** and **6***, that from the MIPA unit (4.0 ppm) for **7***, that from methyl groups from the MKDA unit (3.0 ppm) for **8*** and that from the methyne group of BHTDA for **4***. The composition of each polyimide is comparable with the theoretical composition. The degree of substitution was estimated by means of vinyl protons from MAI, located at 5.7 and 5.9 ppm, against the methyne proton from benzhydrol polyimide visible at 6.25 ppm. The incorporation of a methacryloyl carbamate group was also confirmed by signals at 1.9 ppm (methyl protons), at 11 ppm (carbamate proton) and by the moving of the methyne proton from 6.7 to 7.3 ppm. As an example, the ^{1}H and ^{13}C n.m.r. spectra of **7*** are shown in *Figures 1* and *2*, respectively.

Glass transition temperature. On account of the thermal crosslinkage of the methacryloyl double bond above 100°C, and then of the splitting off of the crosslinking bridges and the depolymerization, the determination of glass transition temperature (T_g) was only carried out on the non-substituted benzhydrol polyimides (**1**, **2**, **3** and **4**) by using d.s.c. The results are given in *Table 4*. Polymers present T_g varying from 210 to 270°C. Benzhydrol polyimides containing a methyl substituted diamine in the *ortho* position have the lowest T_g values, inferring the most flexible molecular backbone. On the other hand, the presence of the hexafluoroisopropylidene group increases the value of T_g, as already reported[17].

Thermal stability. The t.g.a. method was used to examine on the one hand the effect of carbamate groups (*Figure 3a*) and on the other the effect of the alkyl groups (*Figure 3b*) on the thermal stability of polyimide. As a comparison, the t.g.a. of a conventional photosensitive polyamic acid is given in *Figure 3a*.

In *Figure 3a*, the benzhydrol polyimide **1** shows no weight loss below 450°C in nitrogen. Methacryloyl carbamate-modified polyimides **1a*** and **1b*** undergo a rapid degradation above 160°C. The weight loss of the first drop corresponds to the release of the side chain methacryloyl groups and is proportional to the ratio of the methacryloyl carbamate group fixed on the polyimides. The maximum weight loss corresponding to the wholly substituted polyimide carbamate **1a*** is only about 17%. Since our polyimides are fully imidized, the shrinkage during the curing process would be much lower than that of photosensitive polyamic acid. In *Figure 3b*, the presence of methyl groups on the polymer backbone decreases the temperature at which thermal decomposition starts and increases the rate of

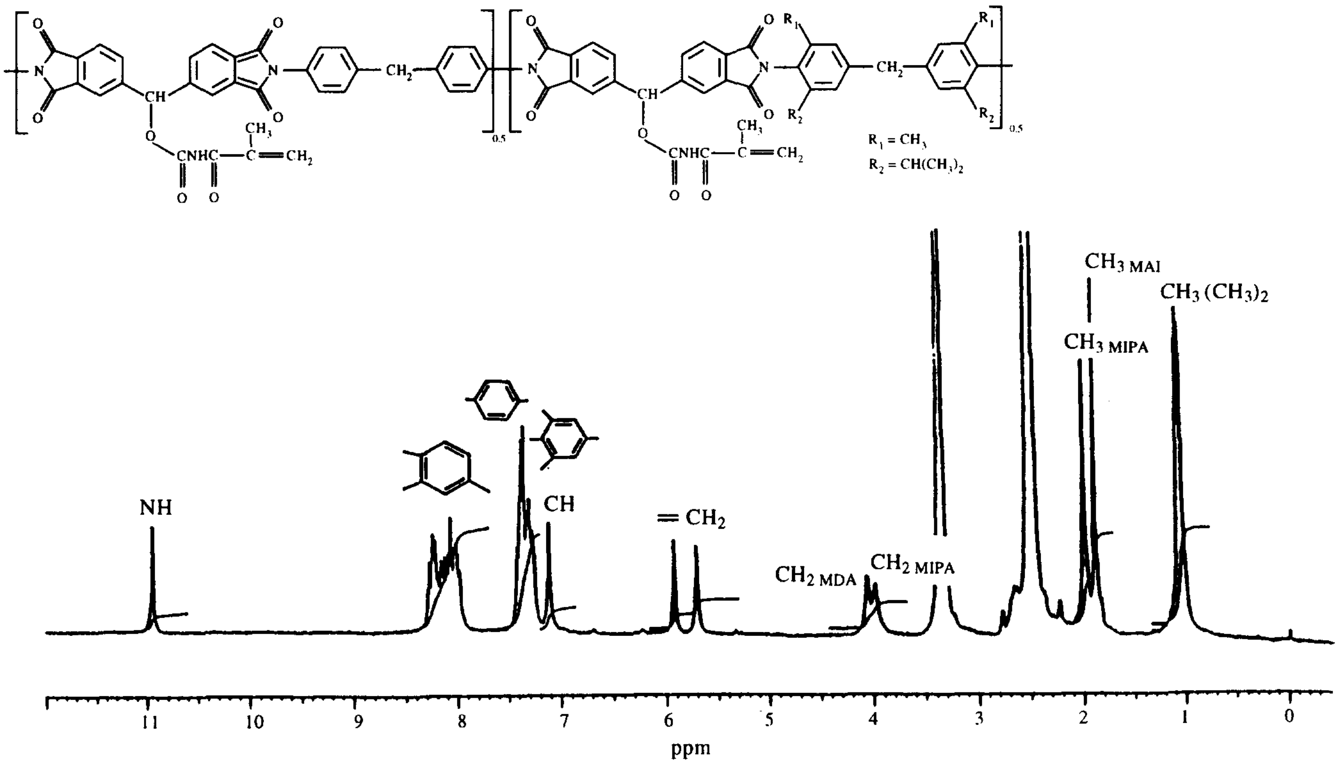


Figure 1 ^{1}H n.m.r. spectrum of 7* (DMSO-d_6)

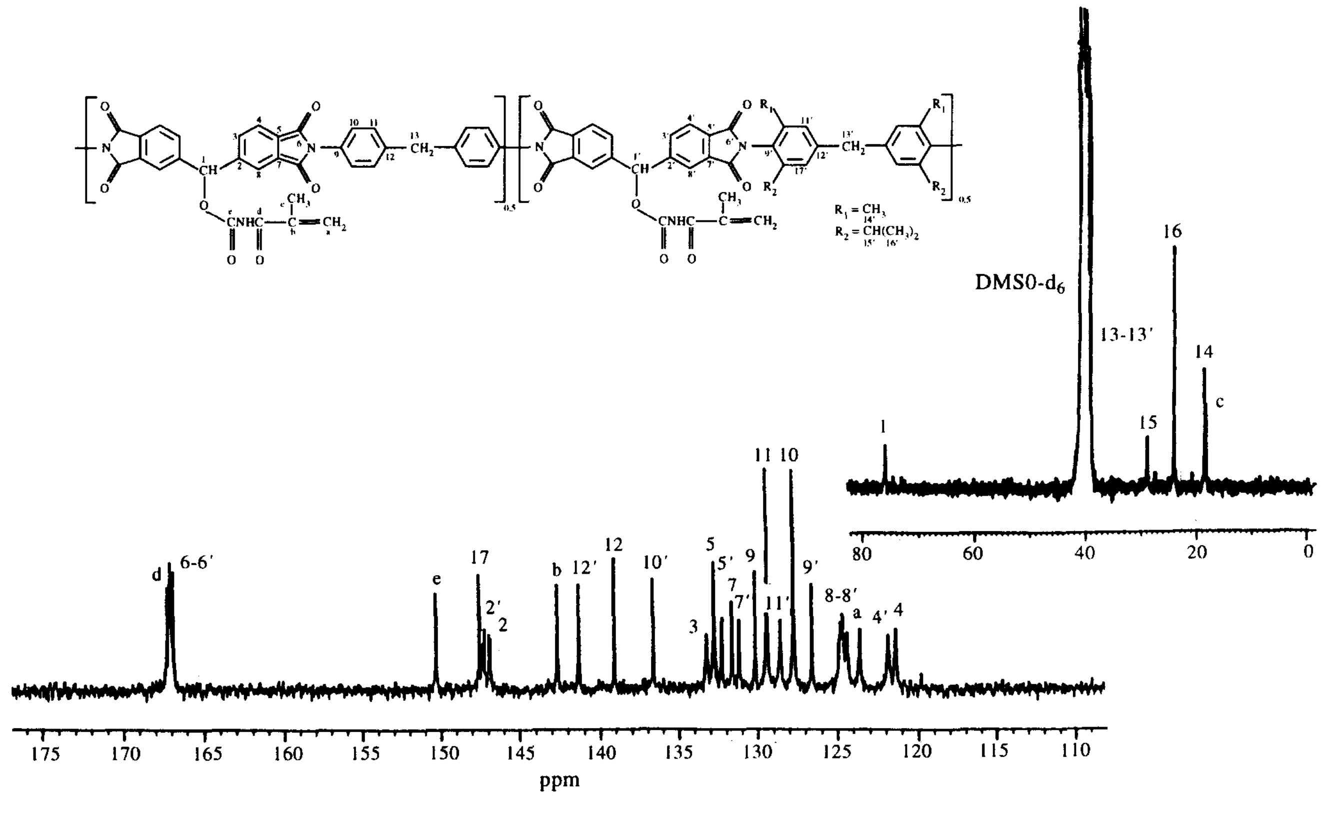


Figure 2 ^{13}C n.m.r. spectrum of 7* (DMSO-d_6)

degradation. However, the number of alkyl substituents seems to have no influence on the thermal stability.

Dielectric constants. The dielectric constants of the benzhydrol polyimide **1** and of the methacryloyl carbamate-modified polyimide **1a*** were determined at 25°C and 1000 MHz. The polyimide carbamate exhibits a dielectric constant (4.2) higher than that of the benzhydrol polyimide (2.9) due to the greater polarity of the photosensitive methacryloyl group.

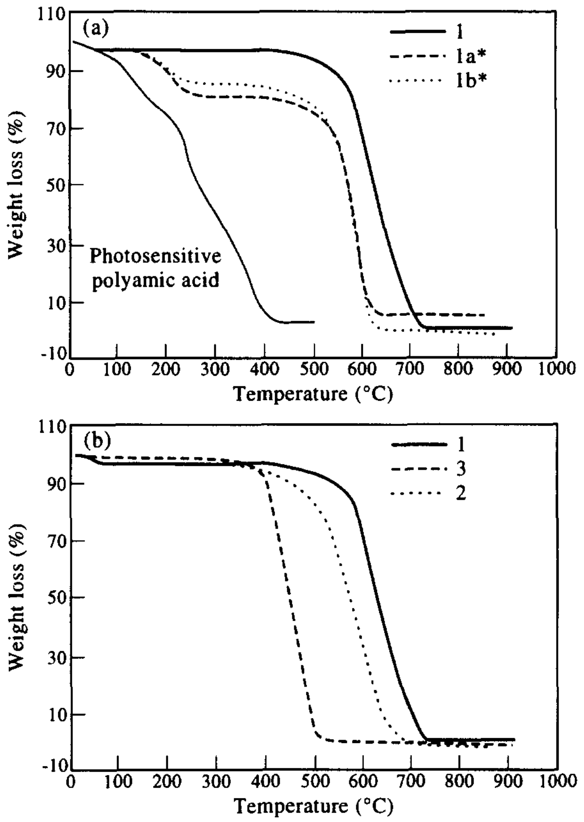


Figure 3 Thermogravimetric curves determined by t.g.a. ($10^{\circ}\mathrm{C\,min^{-1}}$) in nitrogen: (a) effect of carbamate group; (b) effect of alkyl group

CONCLUSION

A series of solvent-soluble negative-type photosensitive fully imidized polyimides based on BHTDA were prepared either by a thermal or a chemical imidization. The photoreactive group is incorporated by reaction between hydroxyl groups from BHTDA or from benzhydrol polyimide and MAI. The resulting photosensitive methacryloyl carbamate-modified polyimides have been found to be soluble in polar solvents, and the expected structure has been confirmed by means of ^{1}H and ^{13}C n.m.r. spectroscopy. These polymers possess an inherent viscosity in the range $0.4-1.0\,\mathrm{dl\,g^{-1}}$, depending on the structure of the polyimide and on the method of imidization used. They exhibit high glass transition temperatures from 210 to 286°C. The imide structure is stable until either 386 or 450°C, depending on the structure of the polyimide. The shrinkage, due to the volatilization of the photoreacted methacryloyl group, is only about 17 wt%, which is much lower than that of conventional photosensitive polyamic acid.

REFERENCES

1. Rubner, R., Ahne, H., Kuhn, E. and Kolodziez, G., *Photogr. Sci. Eng.*, 1979, **33**, 303.
2. Shoji, F., Takemoto, K., Yokono, A. and Isogai, T., Jpn Kokai Tokkyo Koho, 80 45 746, 1980.
3. Hiramoto, H. and Eguchi, M., Jpn Kokai Tokkyo Koho, 79 116 217, 1979.
4. Yoda, N. and Hiramoto, H., *J. Macromol. Sci., Part A*, 1984, **A21**, 1641.
5. Harris, F. W., Feld, W. A. and Lanier, L. H., *Polym. Prepr.*, 1976, **17**, 353.
6. Lee, H. R. and Lee, Y. D., *J. Polym. Sci., Part A*, 1989, **27**, 1481.
7. Nishizawa, H., Suzuki, K., Hagiwara, H. and Kojima, Y., Jpn Kokai Tokkyo Koho, 05 232 701, 1993.
8. Nakano, T., *Proceedings of the International Conference on Polyimides*, Ellenville. New York, 1985, p. 163.
9. Ube Industries, Jpn Kokai Tokkyo Koho, 59 220 730, 1984.
10. Rohde, O., Smolka, P., Falcigno, P. A. and Pfeifer, J., *Polym. Eng. Sci.*, 1992, **32**, 1623.
11. Malinge, J., Garapon, J. and Sillion, B., *Br. Polym. J.*, 1988, **20**, 431.
12. Berrada, M., Carriere, F., Coutin, B., Monjol, P., Sekiguchi, H. and Mercier, R., *Chem. Mater.*, 1996, **8**, 1029.
13. Urano, S., Aoki, K., Tsuboniwa, N., Mizuguchi, R. and Tsuge, O., *Prog. Org. Coat.*, 1992, **20**, 471.
14. Rames-Langlade, G., Monjol, P., Sekiguchi, H., Mercier, R. and Sillion, B., *Macromol. Chem. Phys.*, (Submitted).
15. Yang, C.-P. and Hsiao, S.-H., *J. Appl. Polym. Sci.*, 1985, **30**, 2883.
16. Abajo, J., *Handbook of Polymer Synthesis, Part B*, ed. H. R. Kricheldorf. M. Dekker, New York, 1992, p. 941.
17. Khanna, D. N. and Mueller, W. H., *Polym. Eng. Sci.*, 1989, **29**, 954.