

# Synthesis and Characterization of Poly(methacrylates) Containing Spiroacetal and Norbornene Moieties in Side Chain

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**ABSTRACT:** A four-step synthetic strategy was applied to achieve novel methacrylic monomers. 5-Norbornene-2,2-dimethanol was prepared from a Diels–Alder reaction of cyclopentadiene and acrolein, followed by the treatment of the adduct with an HCHO/KOH/MeOH solution. The resulting 1,3-diol (**1**) was then acetalized with different aromatic aldehydes having OH groups on the ring to produce four spiroacetal derivatives. The reaction of methacryloyl chloride with the phenolic derivatives led to four new methacrylic monomers that were identified spectrochemically (mass, FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy). Free radical solution polymerization was used to prepare novel spiroacetal–norbornene containing polymethacrylates, which were characterized by FTIR and <sup>1</sup>H-NMR spectroscopy and differential scanning calorimetry and thermogravimetric thermal analysis. Gel permeation chromatography was performed to determine molecular weight averages and polydispersity. The polymethacrylate having naphthalenic nuclei was recognized to be the highest molecular weight polymer ( $M_n = 12144$ ,  $\eta_{inh} = 0.80$  dL/g) with the highest thermal stability. All the polymers showed good solubility in a variety of common organic solvents. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 30–38, 2000

**Key words:** 5-norbornene-2,2-dimethanol; spiroacetal–norbornene containing polymer; synthesis; characterization

## INTRODUCTION

Polymers containing spiroacetal units have attracted interest because they have excellent transparency, good mechanical properties, heat and water resistance, and low birefringence.<sup>1–5</sup> Therefore, this class of polymers is considered to be multifunctional and they can be used as heat-resistant materials, curing agents for epoxy resins after functionalization, photomemory disks, and so forth. A literature survey indicated that several articles reported using the norbornene

unit in ring opening metathesis polymerization<sup>6,7</sup> and synthesis of polymers with a bicyclic unit.<sup>8,9</sup> In the latter case Frommelt and coworkers prepared several unsaturated polyesters that were hardened by styrene in the presence of a catalyst to give an alkali-resistant material.<sup>10,11</sup> However, there appears to be no publication on the synthesis of polymers containing a spiroacetal–norbornene unit in the side chain.

Polymers that have their spiroacetal moieties directly connected to a phenylene group, however, have not been process for practical use, because of their insolubility and infusibility from polymer backbone stiffness.<sup>2,3</sup>

So far these problems have been solved by employing flexible linkage or spacers in the rigid polymer main chain,<sup>12,13</sup> nonlinear groups,<sup>14,15</sup> copolymerization for breaking of the regularity of

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the polymer repeating unit,<sup>16</sup> and introduction of side chains onto the polymer backbone.<sup>5</sup>

In the present work we represent another approach to achieve spiroacetal-containing acrylic-based homopolymers. This article deals with the synthesis, characterization, and preliminary properties of some novel polymethacrylates containing spiroacetal and norbornene moieties in the side chain.

## EXPERIMENTAL

### Materials

Salicylaldehyde, *p*-hydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, and vanillin were used as received from Merck chemicals. *p*-Toluene sulfonic acid (Riedel) was purified according to the method described in the literature.<sup>17</sup> Tetrahydrofuran (THF) and toluene were distilled over sodium. Triethylamine was dried with KOH and then distilled. 2,2'-Azobisisobutyronitrile (AIBN) was crystallized from ethanol and stored at 0°C. 5-Norbornene-2,2-dimethanol<sup>18</sup> and methacryloyl chloride<sup>19</sup> were prepared as reported in the literature.

### Measurements

The structures of the compounds were confirmed by a combination of NMR spectroscopy (Bruker AC80 and AM400), IR spectroscopy (Mattson-1000 FTIR), and mass spectrometry (Fisons Instruments Trio 1000).

The molecular weight of the polymers was determined by gel permeation chromatography (Shimadzu GPC) using a Bruker 1000-Å column. GPC measurements were carried out using a differential refractometric detector in toluene at 40°C and a flow rate of 1.0 mL/min. The column was calibrated with a set of monodisperse polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA, PL Laboratories, STA 625) were used for the study of the thermal behavior of the polymers.

The inherent viscosities of the polymers were measured at a concentration of 0.5 g/dL in chloroform at 30°C.

### Synthesis

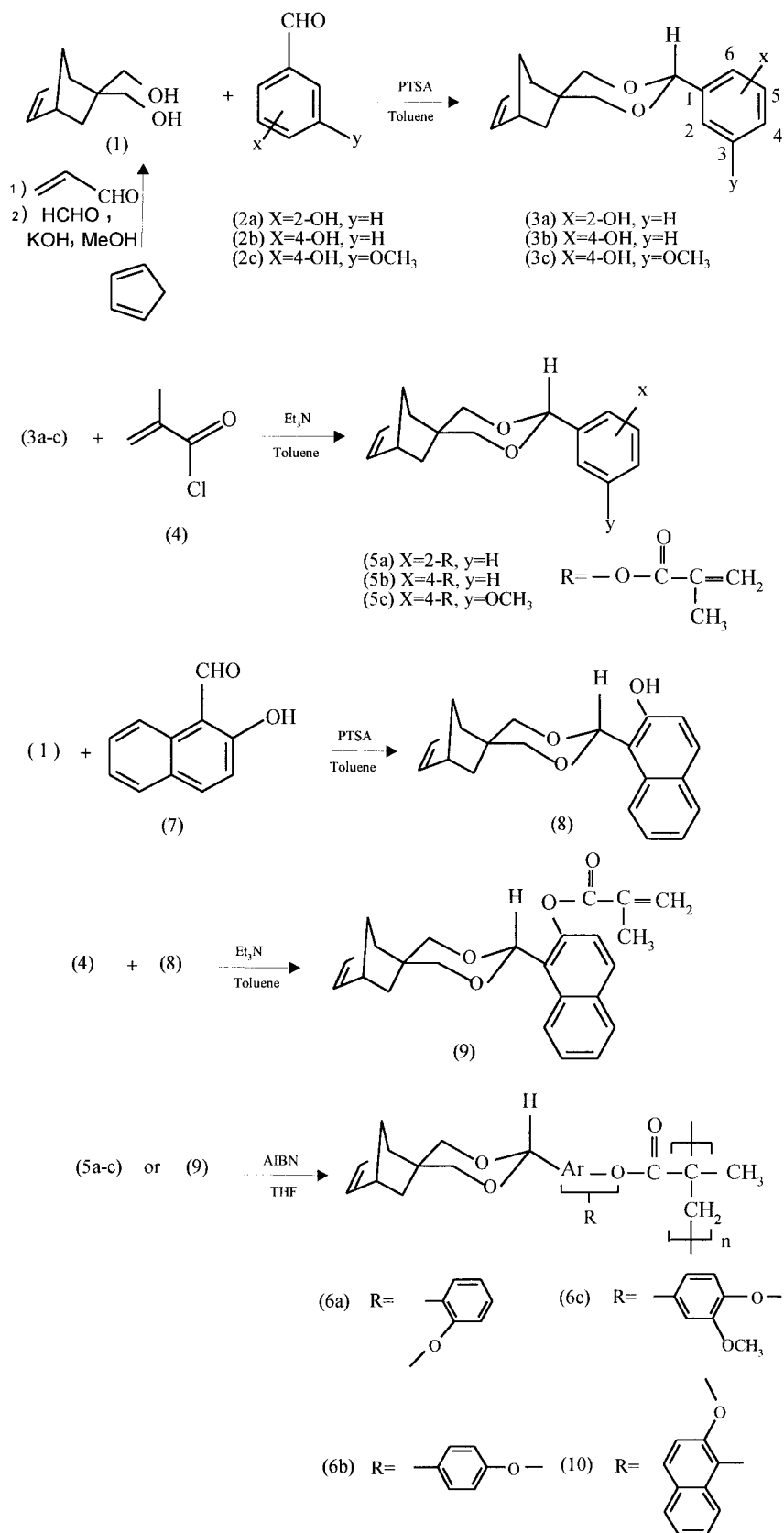
The synthesis of the monomers and polymers is outlined in Scheme 1.

### 5-Norbornene-2,2-dimethanol (1)

5-Norbornene-2-carboxaldehyde (NCA) was prepared from cyclopentadiene monomer and distilled acrolein according to Diels and Alder.<sup>20,21</sup> A mixture of 24.4 g (0.2 mol) of NCA, 44 mL of 35% aqueous formaldehyde (~ 0.5*N*), and 100 mL of methanol was charged into a 250-mL two-neck flask equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel. A 35% potassium hydroxide solution (containing 11.2 g KOH) was added dropwise to the refluxing mixture over a period of 1 h. The reddish brown reaction mixture was refluxed for 2 h and then was allowed to cool to room temperature. Most of the solvent was removed by distillation and the residue was extracted by ether (4 × 20 mL). The combined organic layer was dried over anhydrous magnesium sulfate. The drying agent was filtered off and the filtrate was concentrated under reduced pressure to give a cake, which was recrystallized from benzene (or dichloromethane) to yield 13 g (72.2%) of white needle crystals: mp 112–114°C (lit.<sup>18</sup> 110°C); 400-MHz <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.69 (dd, *J* = 12.7, 3.6 Hz, 1H), 1.28 (dd, *J* = 12.7, 3.6 Hz, 1H), 1.45 (d, *J* = 6 Hz, 1H), 1.53 (d, *J* = 6 Hz, 1H), 2.80 (brs, 1H, >CH—), 2.93 (brs, 1H, >CH—), 3.45 (brs, br, 1H, OH), 3.58 (brs, 2H, —CH<sub>2</sub>O—), 3.81 (brs, 1H, OH), 3.86 (brs, 2H, —CH<sub>2</sub>O), 6.16 (s, 2H, HC=CH) ppm; <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 32.89 (t, —CH<sub>2</sub>—), 42.02 (d, >CH—), 44.60 (d, >CH—), 46.93 (t, >CH<sub>2</sub>, bridge), 48.54 (s, >C<), 69.95 (t, —CH<sub>2</sub>OH, *endo*), 70.85 (t, —CH<sub>2</sub>OH, *exo*), 135.05 and 137.07 (d, —CH=); IR (KBr) 3310, 3050, 2960, 2870, 1630, 1569, 1466, 1413, 1329, 1255, 1018, 932, 714 cm<sup>-1</sup>.

Spiro (1,3-dioxane-norbornene) compounds (**3a–c**, **8**) were synthesized by acetalization of 5-norbornene-2,2-dimethanol with carbonyl compounds (**2a–c** or **7**) and 1% (w/w) paratoluene sulfonic acid (PTSA) (as the catalyst) in toluene for 2 h. This reaction proceeded with the azeotropic removal of water using a Dean–Stark apparatus.<sup>22</sup> The product was crystallized from ethanol and the water mixture. The yield, melting point, NMR, and IR spectroscopic characteristic of **3a–c** and **8** follow.

*Spiro*[1,3-dioxane-5,2'-[5']-norbornene]-2-(*o*-hydroxyphenyl) (**3a**). White crystal, yield 85%, mp 109–111°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 1.2 (brd, *J* = 12 Hz, 1H), 1.4 (brs, 2H), 1.9 (dd, *J* = 12, 3.6 Hz, 1H) 2.3 (brs, 1H), 2.9 (brs, 1H), 3.5–4 (m, 4H,



**Scheme 1** The synthesis of the monomers and polymers.

—CH<sub>2</sub>O—), 5.4 (s, 1H), 5.9 (m, 1H, HC=C—), 6.1 (m, 1H, —C=CH), 6.7–7.3 (m, 4H, ph), 7.7 (s, 1H, OH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 35 (t), 42 (s), 43 (d), 45 (d), 47 (t), 75 (t), 78 (t), 102 (d), 118 (d), 120 (d), 122 (s), 128 (d), 130 (d), 133 (d), 140 (d), 158 (s); IR (KBr): 3338, 1650, 1592, 1500, 1392, 1246–1115, 761 cm<sup>-1</sup>.

*Spiro[1,3-dioxane-5,2'-[5']-norbornene]-2-(p-hydroxyphenyl)* (**3b**). White crystal, yield 80%, mp 149–151°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.5 (brd, *J* = 12 Hz, 1H), 1.0 (dd, *J* = 12, 3.6 Hz, 1H), 1.4 (brs, 2H), 2.7 (brs, 1H), 3.1 (brs, 1H), 3.6–3.8 (m, 4H, —CH<sub>2</sub>O), 5 (s, 1H, OH), 5.3 (s, 1H), 5.9 (m, 1H, —C=CH), 6.1 (m, 1H, H—C=C—), 6.6 (d, *J* = 8.6 Hz, 2H, ph), 7.2 (d, *J* = 8.6 Hz, 2H, ph); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 38 (t), 46 (d), 48 (s), 50 (d), 52 (t), 79 (t), 80 (t), 106 (d), 120 (d), 132 (d), 135 (s), 140 (d), 142 (d), 162 (s); IR (KBr): 3292, 1623, 1523, 1276–1092, 800 cm<sup>-1</sup>.

*Spiro[1,3-dioxane-5,2'-[5']-norbornene]-2-(p-hydroxy-m-methoxyphenyl)* (**3c**). White crystal, yield 80%, mp 101–103°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.5 (brd, *J* = 12 Hz, 1H), 1.2 (dd, *J* = 12, 3.6 Hz, 1H), 1.5 (brs, 2H), 2.7 (brs, 1H), 3.5 (brs, 1H), 3.7 (s, 3H, OCH<sub>3</sub>), 3.5–4 (m, 4H), 5.3 (s, 1H), 5.6 (s, 1H, OH), 6.2 (brs, 2H, HC=CH), 6.9 (m, 3H, ph); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 33 (t), 42 (d), 43 (s), 45 (d), 48 (t), 57 (q), 75 (t), 78 (t), 102 (d), 108 (d), 115 (d), 120 (d), 130 (s), 135 (d), 138 (d), 175 (s), 178 (s); IR (KBr): 3359, 1615, 1523, 1100–1276, 823 cm<sup>-1</sup>.

*Spiro[1,3-dioxane-5,2'-[5']-norbornene]-2-(o-hydroxynaphthyl)* (**8**). White crystal, yield 70%, mp 143–144°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.62 (brd, *J* = 12 Hz, 1H), 1.25 (dd, *J* = 12, 3.6 Hz, 1H), 1.5 (brs, 2H), 2.8 (brs, 1H), 3.4 (brs, 1H), 3.7–3.9 (m, 2H), 4 (brs, 2H), 6.1 (brs, 2H), 6.25 (s, 1H), 7.1–7.8 (m, 5H, naph), 7.7 (s, 1H, OH), 9 (s, 1H, naph); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 32 (t), 41 (d), 43 (s), 45 (d), 47 (t), 74 (t), 76 (t), 102 (d), 110 (s), 120 (d), 122 (d), 124 (d), 125 (s), 127 (d), 129 (d), 131 (d), 132 (s), 135 (d), 138 (d), 155 (s); IR (KBr): 3264, 1630, 1523, 1238–1107, 1007, 753 cm<sup>-1</sup>.

All methacrylate monomers (**5a–c**, **9**) were synthesized from methacryloyl chloride and corresponding phenols (**3a–c**, **8**) with triethylamine as the acid acceptor in the toluene solution. For an example, the synthesis of **5b** is described.

*p*-[2-*spiro*[1,3-dioxane-5,2'-[5']-norbornene]] *Phenyl Methacrylate* (**5b**). A three-necked, 100-mL Claisen flask equipped with a reflux condenser,

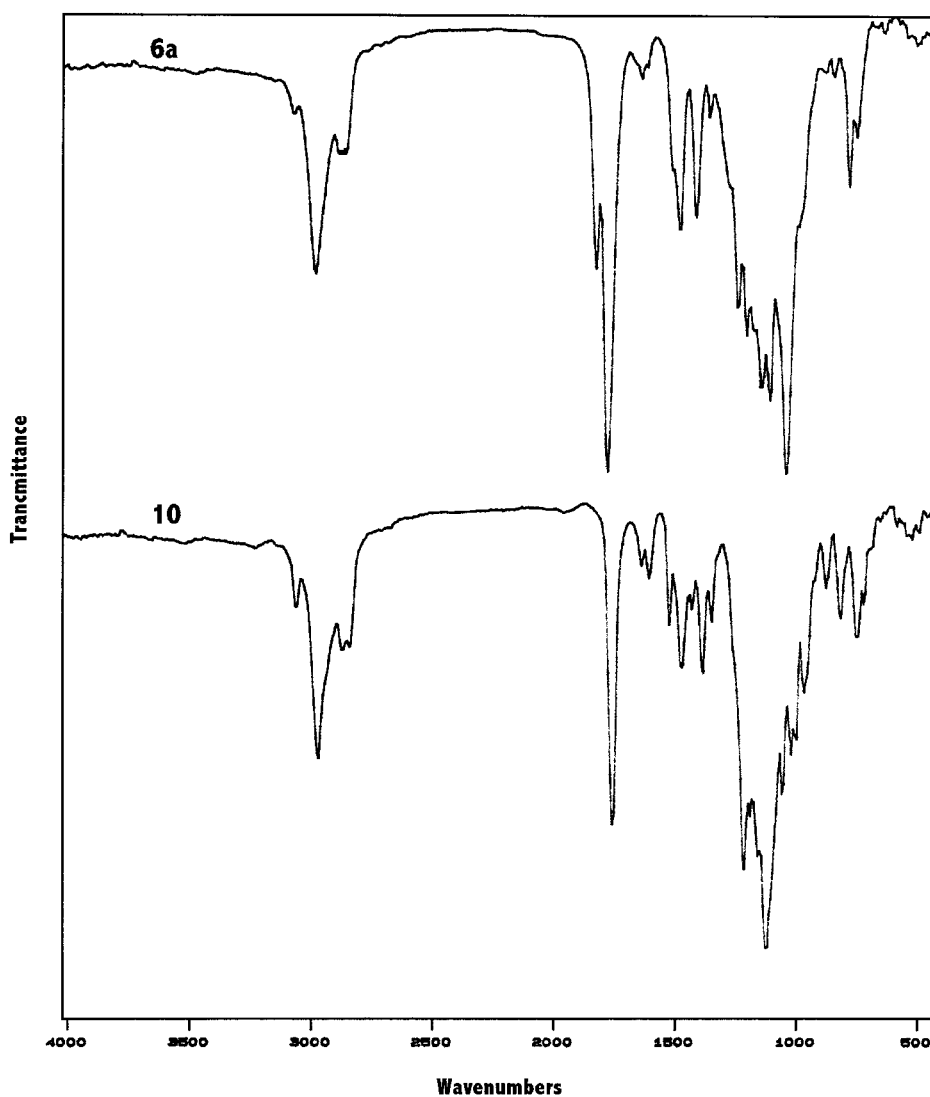
a dropping funnel, and a drying tube was charged with 20 mmol (5.16 mg) of **3b**, 15 mL triethylamine, and 50 mL of toluene; 2.5 mL (25 mmol) of methacryloyl chloride was gradually added to the magnetically stirred solution. The reaction mixture was stirred for 30 min at 10°C and then at room temperature for 3 h. The solution was then poured in 200 mL of water and extracted with diethyl ether (2 × 50 mL). The combined ether extracts were washed with water (2 × 50 mL) and dried over sodium bicarbonate. The solvent was removed at reduced pressure. The resulting solid was purified by column chromatography over silica gel using petroleum ether : ether (9 : 1) as eluent (*R<sub>f</sub>* = 0.75), white solid, yield 84%, mp 70–71°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.5 (brs, *J* = 12 Hz, 1H), 1.1 (dd, *J* = 12, 3.6 Hz, 1H), 1.4 (brs, 2H), 2 (s, 3H), 2.6 (brs, 1H), 3.2 (brs, 1H), 3.5 (s, 1H), 3.6 (s, 1H), 3.9 (brs, 2H), 5.3 (s, 1H), 5.6 (brs, 1H), 6.1 (m, 2H), 6.2 (brs, 1H), 7.1 (d, *J* = 8.6 Hz, 2H, ph), 7.5 (d, *J* = 8.6 Hz, 2H, ph); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 19 (q), 33 (t), 42 (d), 43 (s), 45 (d), 47 (t), 74 (t), 76 (t), 101 (d), 122 (d), 127 (t), 127 (d), 136 (d), 136 (s), 137 (s), 138 (d), 151 (s), 166 (s); IR (KBr): 1730, 1615, 1515, 1200, 1138, 1015, 815 cm<sup>-1</sup>. *M*<sup>+</sup>• = 326. The yield, FT-NMR, FTIR, and mass spectroscopic characteristics of other methacrylate monomers (**5a**, **5c**, **9**) follows.

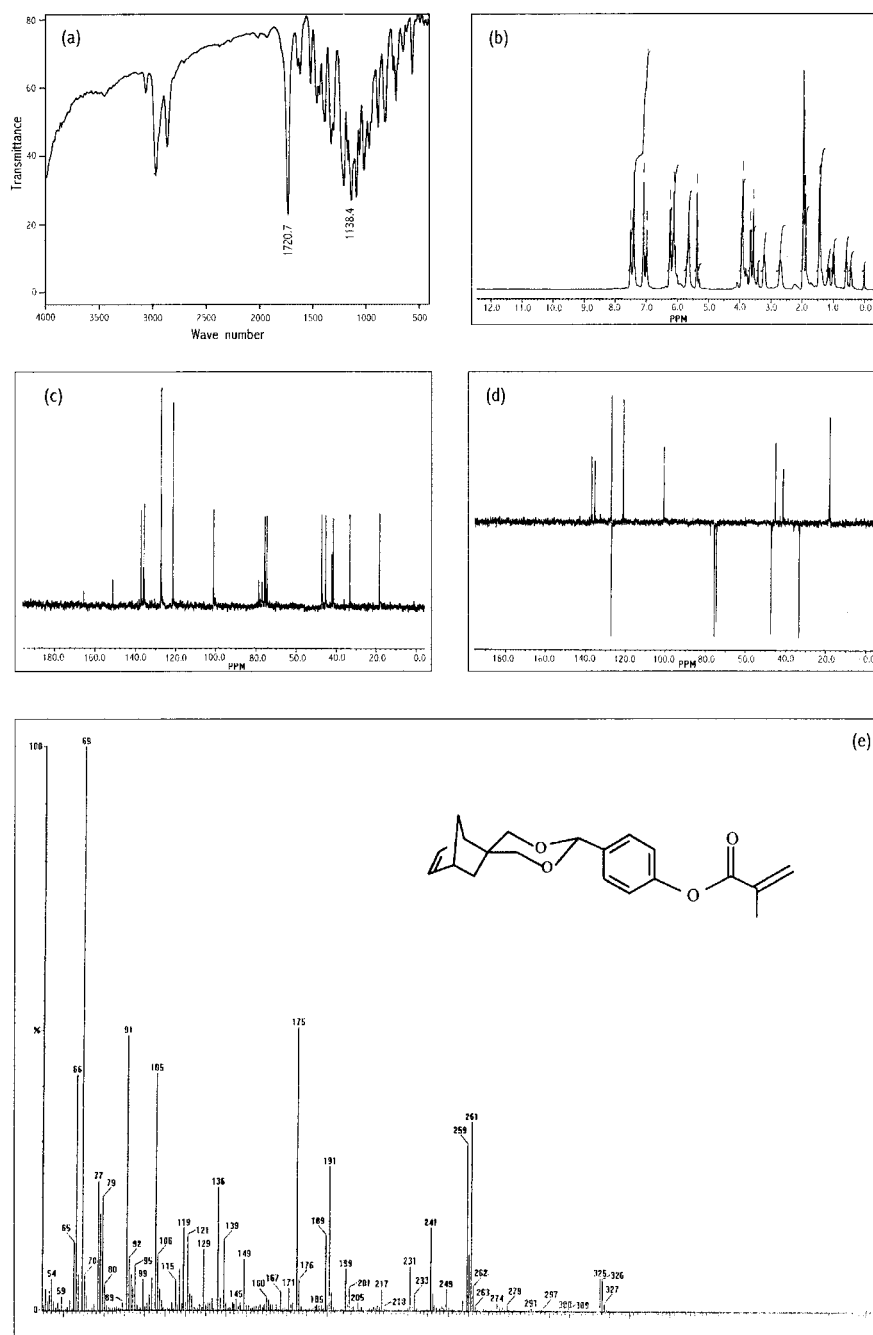
*o*-[2-*spiro*(1,3-dioxane-5,2'-[5']-norbornene)]-*Phenyl Methacrylate* (**5a**). Yellowish oil, yield 66%, mp -8°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 1.3 (brs, 2H), 2 (s, 3H), 1.9–2.1 (m, 2H), 2.6 (brs, 1H), 3.2 (brs, 1H), 3.5 (s, 1H), 3.6 (s, 1H), 3.8 (brs, 2H), 5.4 (brs, 1H), 5.6 (brs, 1H), 5.8 (m, 1H), 6.1 (brs, 1H), 6.3 (brs, 1H), 7–7.5 (m, 4H, ph); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 19 (q), 38 (t), 41 (s), 44 (d), 46 (d), 48 (t), 75 (t), 78 (t), 99 (d), 123 (d), 126 (d), 127 (t), 127 (d), 130 (d), 131 (s), 132 (d), 136 (s), 138 (d), 149 (s), 165 (s); IR (KBr): 1738, 1638, 1500, 1323–1100, 761 cm<sup>-1</sup>. *M*<sup>+</sup>• = 326.

*p*-[2-*spiro*(1,3-dioxane-5,2'-[5']-norbornene)]-*o*-*Methoxy Phenyl Methacrylate* (**5c**). Cream-colored solid, yield 79%, mp 78–80°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.5 (brd, *J* = 12 Hz, 1H), 1.2 (dd, *J* = 12, 3.6 Hz, 1H), 1.4 (brs, 2H), 2 (s, 3H), 2.7 (brs, 1H), 3.2 (brs, 1H), 3.7 (s, 3H, OCH<sub>3</sub>), 3.6–4 (m, 4H), 5.3 (s, 1H), 5.6 (brs, 1H), 6 (m, 1H), 6.1 (m, 1H), 6.3 (s, 1H), 7 (m, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 20 (q), 32 (t), 42 (d), 43 (s), 45 (d), 47 (t), 56 (q), 74 (t), 76 (t), 101 (d), 111 (d), 119 (d), 123 (d), 127 (t), 137 (d), 138 (d), 139 (s), 141 (s), 144 (s), 152 (s),

**Table I** Polymerization Yield and Spectral Data of Polymers

Polymer	Appearance (Yield)	Spectral Data	
		FTIR (KBr) ( $\text{cm}^{-1}$ )	$^1\text{H-NMR}$ ( $\text{CDCl}_3$ ) (ppm)
<b>6a</b>	White solid (56%)	1761, 1607, 1500, 1223, 1123, 1023, 761	$\delta = 0.5-4$ (m, 15H), 5.5 (brs, 1H), 6 (brs, 2H, HC=CH), 6.8-7.8 (m, 4H, ph)
<b>6b</b>	White solid (71%)	1753, 1615, 1515, 1200-1092, 807	$\delta = 0.5$ (brd, 1H), 0.8-2.5 (m, 8H), 2.7 (brs, 1H), 3.3 (s, 1H), 3.6 (brs, 2H, $-\text{CH}_2\text{O}-$ ), 4 (brs, 2H, $-\text{CH}_2\text{O}-$ ), 5.4 (s, 1H), 6.2 (brs, 2H, H-C=CH), 7-7.5 (brs, 4H, ph)
<b>6c</b>	Cream-colored solid (62%)	1753, 1607, 1515, 1284, 1161, 1092, 1030, 807	$\delta = 0.5-4.2$ (m, 18H), 5.3 (S, 1H), 6 (brs, 2H), 7 (brs, 3H)
<b>10</b>	White solid (51%)	1753, 1650, 1600, 1500, 1207, 1123, 746	$\delta = 0.5-4$ (m, 15H), 5.6-6 (brs, 3H), 7.5 (brs, 5H), 8.8 (brs, 1H)

**Figure 1** Typical FTIR spectra of polymers **6a** and **10**.



**Figure 2** (a) FTIR, (b)  $^1\text{H-NMR}$ , (c)  $^{13}\text{C-NMR}$ , (d) DEPT, and (e) mass spectra of monomer **5b**.

165 (s); IR (KBr): 1738, 1607, 1500, 1200, 1138, 807,  $750\text{ cm}^{-1}$ .  $\text{M}^{+\bullet} = 356$ .

*o*-[2-spiro(1,3-dioxane-5,2'-[5']-norbornene)] Naphthyl Methacrylate (**9**). White solid, yield 65%, mp  $132\text{--}134^\circ\text{C}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 0.6 (brd,  $J = 12\text{ Hz}$ , 1H), 1.2 (dd,  $J = 12, 3.6\text{ Hz}$ , 1H), 1.5 (brs, 2H), 2 (s, 3H), 2.7 (brs, 1H), 3.5 (brs, 1H),

3.6–4 (m, 4H), 5.7 (brs, 1H), 6–6.4 (m, 4H), 7–7.8 (m, 5H), 8.8 (m, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 20$  (q), 34 (t), 42 (d), 43 (s), 47 (d), 48 (t), 75 (t), 77 (t), 100 (d), 121 (d), 123 (s), 125 (d), 126 (d), 127 (d), 128 (t), 129 (d), 131 (d), 132 (s), 133 (s), 136 (d), 136 (s), 138 (d), 148 (s), 166 (s); IR (KBr): 1730, 1630, 1600, 1500, 1215, 1138, 1007,  $753$ .  $\text{M}^{+\bullet} = 376$ .

**Table II Solubility of Polymers**

Polymer	Solvent									
	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	THF	DMF	DMAc	NMP	DMSO	Ph-Me	Acetone	Acetonitrile
<b>6a</b>	+	+	+	+	+	+	+	+	+	+
<b>6b</b>	+	+	+	+	+	+	+h	+	-	-
<b>6c</b>	+	+	+	+	+	+	+h	+	-	+h
<b>10</b>	+	+	+	+	+	+	+h	+	-	-

+, soluble at room temperature; +h, soluble on heating; -, insoluble; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulfoxide; DMF, *N,N*-dimethyl formamide; DMAc, *N,N*-dimethyl acetamide; THF, tetrahydrofuran; Ph-Me, toluene.

## Polymerization

Polymerization of the synthesized monomers (**5a–c**, **9**) was carried out via a free radical solution polymerization in THF using AIBN as the initiator. The concentration of monomers and the initiator was 10% (w/v) and 2 mol %, respectively. As an example for a general polymerization procedure, the synthesis of the polymer from **5b** is given below.

*Poly{p-[2-spiro(1,3-dioxane-5,2'-[5']-norbornene)]-Phenyl Methacrylate} (**6b** from **5b**)*. An amount of 1.25 g (4 mmol) of **5b** and 13 mg of AIBN were dissolved in 12.5 mL of THF. The reaction mixture was purged with a gentle stream of nitrogen. The mixture was heated at 60°C for 6 h. The resulting homogeneous solution was cooled and added dropwise into 200 mL of diethyl ether to precipitate the polymer. The polymer was dried at 50°C in a vacuum for 18 h.

The cast films of all polymers in chloroform were clear and brittle. Polymerization yield, IR, and <sup>1</sup>H-NMR spectral data of the polymers are summarized in Table I. In addition, typical FTIR spectra of **6a** and **10** are shown in Figure 1.

## RESULTS AND DISCUSSION

### Monomer and Polymer Synthesis

A known two-step trajectory was followed to prepare diol **1**. A facile high yield Diels–Alder reaction between cyclopentadiene and acrolein produced NCA. The latter was then treated with formalin solution in methanolic potassium hydroxide at reflux conditions. An aldol condensation followed by a Cannizzaro reaction occurred to yield the 1,3-diol **1** (Scheme 1).

Spiro(1,3-dioxane-norbornene) derivatives (**3a–c**, **8**) were synthesized through the acid-catalyzed acetalization of **1** and the corresponding aromatic

aldehydes (Scheme 1). The reactions yielded 70–85% white crystals. The spectral data of these derivatives are summarized in the Experimental section. Acetal formation was confirmed by an FTIR absorption band at ~ 1100 cm<sup>-1</sup> (C—O—C stretching) and by a deshielded hydrogen at ~ 5.5 ppm in the <sup>1</sup>H-NMR spectra. The absorption bands at about 0.5, 1, 1.4, 2, 2.7, 3.2, and 6.2 ppm are all due to the norbornene unit. Substituted phenolic (**3c**) was discriminated from the unsubstituted phenolics by either the quartet peak in <sup>13</sup>C-NMR at 57 ppm or the singlet peak in <sup>1</sup>H-NMR at 3.7 ppm, which are due to the OCH<sub>3</sub> group.

The new methacrylic monomers were synthesized by esterification of the spiroacetal compounds having phenolic functional groups (**3a–c**, **8**) and methacryloyl chloride in the presence of Et<sub>3</sub>N as an acid acceptor. The products were 65–80% solid or oily substances, which were chromatographically purified. Comparison of the FTIR spectra clearly showed that the phenolic OH stretching broad bands of the phenolic derivatives (**3a–c**, **8**) disappeared and some new strong bands in the region of 1000–1200 cm<sup>-1</sup> (due to esteric C—O—C stretching) and ~ 1730 cm<sup>-1</sup> (due to C=O stretching of the conjugated ester) appeared.

The <sup>13</sup>C-NMR spectra indicate C=O, =CH<sub>2</sub>, and CH<sub>3</sub> at ~ 166, ~ 127, and ~ 20 ppm, respectively. In addition, the most stable fragment (base peak) in the mass spectra was due to the methacrylate group (*m/z* 69).

Figure 2 shows FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR distortionless enhancement of polarization transfer (DEPT), and mass spectra of monomer **5b**. Free radical polymerization (AIBN, THF, 60°C, 6 h) was applied to prepare the homopolymers. White or cream-colored solid polymers were obtained (Table I). As evidence of polymer formation, C=O stretching of the nonconjugated esteric bond appeared at 1753–1761 cm<sup>-1</sup> in the FTIR spectra

**Table III** Molecular Weight and Thermal Properties of Polymers

Polymer	GPC <sup>a</sup>				$\eta_{inh}^b$ (dL/g)	DSC-TG		
	$R_t$ (min)	$M_n$	$\bar{M}_w/\bar{M}_n$	$\overline{DP}_n$		$T_g$ (°C)	PDT (°C)	$T_{10}$ (°C)
<b>6a</b>	7.20	1495	1.84	4.60	0.68	—	257.2	280
<b>6b</b>	5.58	4809	1.53	14.8	0.72	209.05	280.0	320
<b>6c</b>	6.73	2275	1.88	6.40	0.71	206.50	278.8	315
<b>10</b>	5.83	12144	1.52	32.3	0.80	—	312.0	320

$T_g$ , the glass transition temperature; PDT, the polymer decomposition temperature; DSC-TG, the DSC under Ar at a heating rate of 10°C/min;  $T_{10}$ , the temperature at 10% weight loss.

<sup>a</sup> Determined by GPC in toluene using a polystyrene standard at 40°C.

<sup>b</sup>  $c = 0.5$  g/dL in  $CHCl_3$  at 30°C.

(Fig. 1). In  $^1H$ -NMR the  $\begin{matrix} \diagup \\ -C-CH_2 \\ \diagdown \end{matrix}$  units of the polymer main chain were located at 1–1.5 ppm. Other bands were the same as the corresponding monomers.

### Polymer Solubility

It is known that wholly aromatic polyspiroacetals are insoluble in common organic solvents. Therefore, they could not be processed for practical use.

The solubility of polymers (at 25% w/v) is indicated in Table II. All of the polymers obtained in this work were soluble in  $CHCl_3$ ,  $CH_2Cl_2$ , THF, *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and *N,N*-dimethylacetamide (DMAc) at room temperature.

The **6a** was completely dissolved in common solvents due to its unsymmetrical structure. But, in spite of an unsymmetrical structure for **10**, it did not dissolve in polar solvents such as acetonitrile and acetone, which may be attributed to the heavy rigid naphthalenic nuclei. However, it was dissolved in amide-type solvents such as NMP, DMAc, and DMF. The solubility of **6b** and **6c** was limited by their symmetric structure; so, they did not dissolve in DMSO, acetone, and acetonitrile at room temperature.

### Polymer Molecular Weight and Thermal Behavior

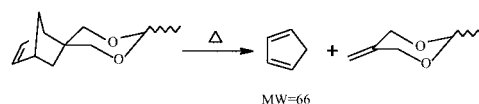
The molecular weight of the polymers was determined by GPC and the thermal properties were evaluated by DSC and TGA at a heating rate of 10°C/min (Table III).

As indicated in Table III, the highest and lowest average molecular weights and inherent viscosity are concerned with **10** and **6a**, respectively. The preparation yield of **6a** and **10** were the two lowest as well (Table I). This may be attributed to a trace of impurity in the oily corresponding

monomer, **5a**, which had been purified with much difficulty. It may have also come from the fact that the methacrylate group is ortho to the spiroacetal, causing steric hindrance at the reactive center. On the other hand, **10** may not be comparable to the other polymers from this point of view, because of the presence of the different aromatic structures (naphthalenic nuclei) in the side chain.

The TG traces indicate that all the polymers possess low to medium thermal stability under an inert atmosphere. All the TGA thermograms showed a partial step decomposition. Such a thermal decomposition pattern can be accurately attributed to a retro-Diels–Alder (endothermic) reaction occurring at 300–400°C to eliminate cyclopentadiene (Scheme 2). In the case of **6b**, for instance, the weight loss was calculated to be 20% [(66/326)100 = 20%], which is the same as resulted from its TGA curve (Fig. 3).

As expected, **10** showed the highest polymer decomposition temperature (PDT), which is due to the highest rigidity of its aromatic component. The temperature at 10% weight loss, as well as the PDT, of **6a** were the lowest quantities, because of its relatively low molecular weight. In spite of a long thermal period (18 h at 50°C) under a vacuum, the TGA curves of **6a** and **10** showed a small weight loss (1–2 wt %) range at 130–190°C, which may be attributed to a loss of the residual moisture. No melting transition was observed for the polymers according to the DSC analysis.



**Scheme 2** The thermal decomposition pattern from a retro-Diels–Alder endothermic reaction.



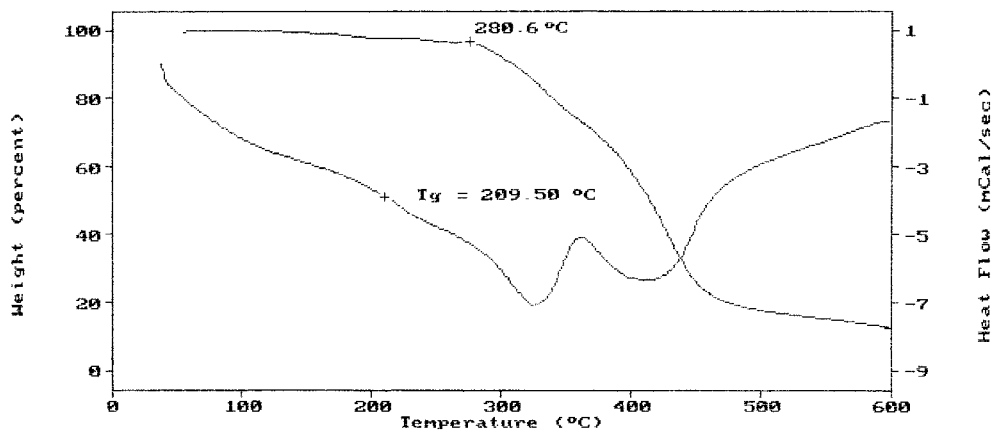


Figure 3 DSC-TG thermogram of polymer **6b**.

Moreover, no glass transition temperature was recorded for **6a** and **10**.

A representative DSC-TG thermogram of polymer **6b** is given in Figure 3.

## CONCLUSION

Four novel soluble polymethacrylates containing a spiroacetal-norbornene moiety in the side chain were synthesized by free radical solution polymerization. The corresponding new methacrylic monomers were prepared through a four-step pathway that started from cyclopentadiene and acrolein. The monomers and homopolymers were characterized by spectroscopy, size exclusion chromatography, and thermoanalytical techniques accordingly. We recognized **10** as the most thermally stable polymer. The presence of a double bond in the norbornene moiety caused the polymers to be good candidates for chemical modification (e.g., reduction, oxidation by ozonization, epoxidation, addition, and crosslinking reactions). So, these polymers include potential structural components to convert to higher performance materials.

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