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Polymer 45 (2004) 2111–2117

polymer

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Forgotten monomers: free radical polymerization behavior of norbornadiene derivatives in comparison with methyl methacrylate

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Received 4 December 2003; received in revised form 21 January 2004; accepted 29 January 2004

Abstract

The free radical polymerization behavior of three norbornadiene derivatives was studied as a function of their structure. The compounds examined were 3-ethoxycarbonyl-tricyclo[3.2.1.0^{2,4}]oct-6-ene **1** (liquid), 2-carbethoxybicyclo[2.2.1]-2,5-heptadiene **2** (liquid) and 2-carboxybicyclo[2.2.1]-2,5-heptadiene **3** (solid). They were polymerized in bulk and in benzene solutions. The tricyclic compound **1** was the least reactive monomer whereas the bicyclic derivatives **2** and **3** readily polymerized radically to high conversions. The corresponding polymers were isolated and their structure were determined by means of IR- and NMR spectroscopy. The polymerization of 3-ethoxycarbonyl-tricyclo[3.2.1.0^{2,4}]oct-6-ene **1** is supposed to proceed through a simultaneous ring opening–ring closing mechanism. The corresponding polymer poly-**1** shows low molecular weights. The polymerization results were compared with those obtained for a conventional solution polymerization of methyl methacrylate.

Keywords: Norbornadiene derivatives; Radical polymerization; kinetics

1. Introduction

During the last few years much attention has been addressed to the polymerization of norbornadiene (NBD) and its derivatives, due to novel properties of these materials especially in optical applications. These monomers can be converted in cycloaliphatic polyolefins with 2,6-disubstituted nortricyclene units by transannular isomerization polymerization utilizing conventional carbocationic and radical initiators [1–10]. Carbocationic polymerization of unsubstituted NBD with $AlCl_3$-based initiators was pioneered by Kennedy et al. [1,2] who showed that a very low reaction temperature is required to produce a soluble polymer. More recently, these authors found the specific reaction conditions under which the polymerization of NBD mediated by 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ system gives polymers with a well-defined microstructure by living mechanism [3]. Various catalytic systems such as $AlBr_3$ [4], $EtAlCl_2$/*t*-BuCl [5] and $MoCl_5$/$EtAlCl_3$ [6] have been used for cationic polymerizations of NBD. Anionic polymerization was first reported by Balcioglu and Tunoglu when a crystalline polymer showing higher stability and high molecular weight was formed [7].

Radical polymerization of NBD and NBD derivatives was initially disclosed in publications by Graham and Wiley [8,9]. They outlined the essential aspects of the free radical transannular polymerization of NBD and showed that these polymers contain saturated nortricyclene repeating units and a considerable proportion of unsaturated bicyclic units. Since 1960's, free radical polymerization of NBD derivatives was 'forgotten' and only recently Frechet reported on the radical polymerization of norbornadiene substituted with bulky ester groups. According to them, the ring-closing cyclopolymerization takes place instead of normal vinyl addition for such monomers, being suggested that the resulting polymers containing nortrycyclene units could be successfully applied as photoresist materials in state-of-the art 193-nm microlitography [10]. However, systematic investigations on the polymerizability of substituted norbornadienes have not been reported up to now. Thus, we want to report in the present work a comparison of the radical bulk and solution polymerizations of three

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0032-3861/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.01.056

norbornadiene derivatives to that of methyl methacrylate as a reference monomer.

Compound **1** is a tricyclic olefin that can be converted by ring opening metathesis polymerization into relatively high molecular weight linear polyalkenylenes with pendant ester groups using suitable metathesis-initiators (i.e. WCl_6/$(CH_3)_4Sn$) [11]. Ring opening radical polymerization renders this monomer suitable for dental applications and the tricyclic repeat units of the coresponding polymer are regarded as a potential solar energy storage device. Up to now, radical ring opening polymerization of this monomer was not reported. In this study, we tried to prepare for the first time polynortricyclene derived from 3-ethoxycarbonyl-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene using a radical initiator and to examine the structure of the polymer formed. The preliminary mechanistic results for the polymerization of the tricyclic compound, in terms of structure of the resulting polymer, are discussed. The monomer conversion was investigated by UV–vis spectroscopy and compared with that of methyl methacrylate.

2. Experimental section

2.1. Chemical reagents and measurements

Methyl methacrylate (MMA, Acros), cyclopentadiene (dicyclopentadiene, Acros) and 2,5-norbornadiene (98% purity, Aldrich) were purified by distillation under vacuum just before usage. The catalysts $Pd(OAc)_2$ (Fluka), $Rh(OAc)_2$ (Fluka), CuCN (99.99% purity, Aldrich) and the initiators 2,2′-azobis(2-methylpropionitrile) (AIBN, 98% purity, Acros), benzoyl peroxide (BP, Fluka) were used as received. THF (p.a., Acros), the solvent for kinetic measurements, was refluxed and distilled over calcium hydride. Ethyl diazoacetate (EDA, Aldrich), ethyl propiolate (Acros), benzene (p.a., Acros) and hexane (p.a., Acros) were used without further purification.

Gel permeation chromatography (GPC) analyses of the molecular weight distributions of the polymers were performed using a PSS apparatus with a Shodex refractive index (RI) detector and a TPS UV2000 UV–Vis detector at 25 °C under the following conditions: PSS-SDV (5 μm, 10^3 Å, $8 \times 50\ mm^2$) and 3 PSS-SDV (5 μm, $8 \times 300\ mm^2$ with 10^2, 10^3 and 10^4 Å porosity) columns, THF eluent containing LiBr at a flow rate of 1.0 ml/min. Calibration was done with polystyrene (PSS) standards with a molecular weight range from 374 to 1×10^6 D. Fourier transform infrared (FTIR) spectra of the samples were measured on a Nicolet 5SXB FTIR spectrophotometer. UV spectra were recorded in THF using the UV 540 system of the company Unicam. Differential scanning calorimetry was carried out with a Perkin–Elmer DSC 7 (5 °C/min). Mass spectra were recorded on a Varian MAT 311A instrument. All NMR experiments were performed on a Bruker DRX500 NMR spectrometer or Bruker AC200 FT-NMR with tetramethylsilane as internal standard in chloroform-*d* ($CDCl_3$) or dimethylsulfoxide-d_6 (DMSO-d_6) as solvents. $^1H-^1H$ correlation spectroscopy (COSY), two-dimensional total correlation spectroscopy (TOCSY) and heteronuclear multiple bond correlation (HMBC) were used to assign the resonances of polymer poly-**1**.

2.1.1. Preparation of 3-ethoxycarbonyl-tricyclo [3.2.1.$0^{2,4}$]oct-6-ene *1*

3-Ethoxycarbonyl-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **1** was synthesized according to a slightly modified method of Sauers and Sonnet [12] reported for the cyclopropanation of norbornene with ethyldiazoacetate (EDA). $Pd(OAc)_2$, $Rd(OAc)_2$ and CuCN were used as catalysts. As an example, the synthesis using CuCN is described here in detail. Distilled norbornadiene (19.3 g, 209 mmol) was dissolved in a mixture of catalyst (0.78 g, 8.7 mmol) and hexane (50 ml). The mixture was stirred magnetically and refluxed at 60 °C for 30 min. Then, EDA (19.8 g, 174 mmol) was added dropwise within 1 h. The catalyst/EDA molar ratio was 0.05/1. The mixture was refluxed for further 2 h after complete addition of EDA. The resulting solution was cooled to room temperature, filtered and the filtrate was two times distilled through a fractional column to remove the unreacted reactants, the bisadduct and diethyl maleate/fumarate. The purification by distillation gave 17.2 g (56% yield) of the desired product **1** at 70 °C/10^{-3} mbar.

1. ^1H NMR ($CDCl_3$): $\delta = 6.35$ (dd, exo, 1H, $J = 3.5$ Hz), 5.76 (dd, endo, 0.43H, $J = 3.5$ Hz), 4.02 (d, exo, 2H, $J = 1.9$ Hz), 2.87 (d, endo, 0.43H, $J = 1.9$ Hz), 2.84 (m, exo, 1H), 2.46 (d, endo, 0.86H, $J = 2.53$ Hz), 1.95 (d, endo, 0.86H, $J = 6.6$ Hz), 1.83 (d, endo, 0.86H, $J = 1.6$ Hz), 1.61 (m, endo, 0.43H), 1.58 (d, exo, 2H, $J = 2.2$ Hz), 1.33 (d, exo, 1H, $J = 2.2$ Hz), 1.17, (m, endo and exo, 4.29H), 1.04 (m, exo, 1H), 0.93 (m, exo, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 172.3$ (endo and exo, –CO–), 142.3 (exo, –CH=CH–)), 132.1 (endo, –CH=CH–), 64.6 (endo, $-CH_2-$), 60.6 (endo and exo, $-OCH_2-$), 43.4 (endo, CH), 42.2 (exo, CH), 40.2 (exo, $-CH_2-$), 32.3 (endo and exo, $-CH_3$), 31.8 (endo, CH), 23.4 (exo, CH), 14.6 (endo and exo, CH). FTIR (diamond): $\nu = 3059$, 2980, 1723, 1646, 1475, 1401, 1383, 1295, 1232, 1173, 1099, 1028, 955, 800 cm^{-1}. MS(EI): $m/z = 178[M^+]$, calcd for $C_{11}H_{14}O_2$: 178.23; found 178.29.

2.1.2. Preparation of 2-carbethoxybicyclo[2.2.1]-2,5-heptadiene *2* and 2-carboxybicyclo[2.2.1]-2,5-heptadiene *3*

2-Carbethoxybicyclo[2.2.1]-2,5-heptadiene **2** was synthesized according to a modified method reported by Graham and Pappas [8]. Freshly distilled cyclopentadiene (14 g, 0.212 mol) was added to a solution of ethylpropiolate (17.2 g, 0.176 mol) in 20 ml benzene. The mixture was heated under stirring at 60 °C for 24 h. Any unreacted reactants and solvent were removed under reduced pressure and the remaining mixture was distilled at 5×10^{-3} mbar giving 17.3 g (60% yield) of product **2**. A reported method by Nakatsuji was employed for the synthesis of 2-carboxybicyclo[2.2.1]-2,5-heptadiene **3** [13]. The product was purified by recrystallization from water (36% yield).

2. ^{1}H NMR (CDCl$_3$): $\delta = 7.65$ (d, 1H, $J = 3.2$ Hz), 6.93 (dd, 1H, $J = 3.2$ Hz), 6.74 (dd, 1H, $J = 3.2$ Hz), 4.23 (q, 2H, $J = 21.4$ Hz), 3.90 (s, broad, 1H), 3.70 (s, broad, 1H), 2.17 (m, 2H), 1.26 (t, 3H). ^{13}C NMR (CDCl$_3$): $\delta = 165.5$ (C=O), 155.0 (C=C–), 148.8, 143.1 (C=C), 141.2 (C=C), 74.3, 60.1, 50.5, 50.0, 13.8. MS(EI): $m/z = 164$[M$^+$], calcd for $C_{10}H_{12}O_2$: 164.20; found 164.31.

3. ^{1}H NMR (CDCl$_3$): $\delta = 7.75$ (d, 1H, $J = 3.2$ Hz), 6.85 (dd, 1H, $J = 3.2$ Hz), 6.66 (dd, 1H, $J = 3.2$ Hz), 3.82 (s, broad, 1H), 3.67 (s, broad, 1H), 2.10 (m, 2H). ^{13}C NMR (CDCl$_3$): $\delta = 165.8$ (C=O), 155.3 (C=C–), 150.2, 143.7 (C=C), 142.5 (C=C), 74.3, 51.4, 49.5. FTIR (diamond): $\nu = 3002$, 1652, 1587, 1554, 1412, 1284, 1159 cm^{-1}. MS(EI): $m/z = 136$[M$^+$], calcd for $C_8H_8O_2$: 136.15; found 136.20.

2.1.3. Solution polymerization

A three-necked flask, fitted with stirrer and nitrogen inlet, was evacuated and filled with nitrogen three times. As a typical example, we present only one of the solution polymerization. The conditions and yields for all other polymerizations are given in Table 3. Monomer **1** (0.5 g, 2.8 mmol) was solved in 1.1 ml benzene and the solution was heated at 65 °C. To start the polymerization, 2 mol% AIBN (9.2 mg, 0.056 mmol) was added under gentle stream of nitrogen. The polymerization was terminated after 22 h by pouring the reaction mixture into hexane. The precipitated polymer was filtered off, dried in vacuum and analysed.

2.1.4. Bulk polymerization

In a degassed glass tube 0.5 g (2.8 mmol) of monomer **1** and 0.03 g (0.125 mmol) of BP (5 mol%) were introduced. The tube was sealed under nitrogen atmosphere and placed in a constant temperature bath (80 °C). After 20 h, the resulting polymer was dissolved in chloroform and precipitated in hexane.

Poly-**1**. ^{1}H NMR (CDCl$_3$): $\delta = 0.77–2.42$ (m, 14H), 1.17 (s broad, 3H), 4.01 (m, 2H); ^{13}C NMR (CDCl$_3$): 171.9, 60.4, 48.9, 48.0, 47.0, 26.3, 22.3, 22.0, 17,1, 16.8, 14.0. FTIR (diamond): $\nu = 2973$, 1715 (C=O), 1450, 1264, 1172, 1026, 840 cm^{-1}. GPC data are given in Table 2. DSC: $T_g = 136$ °C.

Poly-**2**. ^{1}H NMR (CDCl$_3$): $\delta = 0.80–2.36$ (m, 10H), 4.01 (m, 2H); ^{13}C NMR (CDCl$_3$): $\delta = 173.7$, 60.3, 49.4, 45.1, 39.8, 33.5, 31.9, 28.0, 27.2, 14.6. FTIR (diamond): $\nu = 2975$, 1712 (C=O), 1464, 1397, 1300, 1169, 1083 cm^{-1}. GPC data are given in Table 2. DSC: $T_g = 27$ °C.

Poly-**3**. ^{1}H NMR (DMSO-d_6): $\delta = 0.93–2.12$ (m, 6H), 3.14 (s broad, 1H), 11.67 (s broad, 1H); ^{13}C NMR (DMSO-d_6): $\delta = 179.8$, 53.3, 51.1, 44.9, 33.1, 31.6, 31.2, 25.3. FTIR (diamond): $\nu = 3316$, 2964, 1682, 1417, 1237, 1172, 1123 cm^{-1}. GPC data are given in Table 2. DSC: $T_g = 82$ °C.

2.2. Kinetic measurements

Polymerizations were performed in THF, under the same conditions mentioned for solution polymerization. Aliquots of 5 ml of the initial solutions were pipetted into seven tubes and the tubes were sealed under nitrogen atmosphere. The ampoules thus prepared were kept simultaneously in a thermostated oil bath. After a certain time, a sample was taken and the UV spectrum of the residual monomer fraction was recorded.

For gravimetric determination of conversion, the samples were taken at the certain time and quenched with precooled hexane. The precipitated polymer was filtered off, washed several times with THF, dried in vacuum and analysed. The complete removal of monomer was verified by ^{1}H NMR.

3. Results and discussion

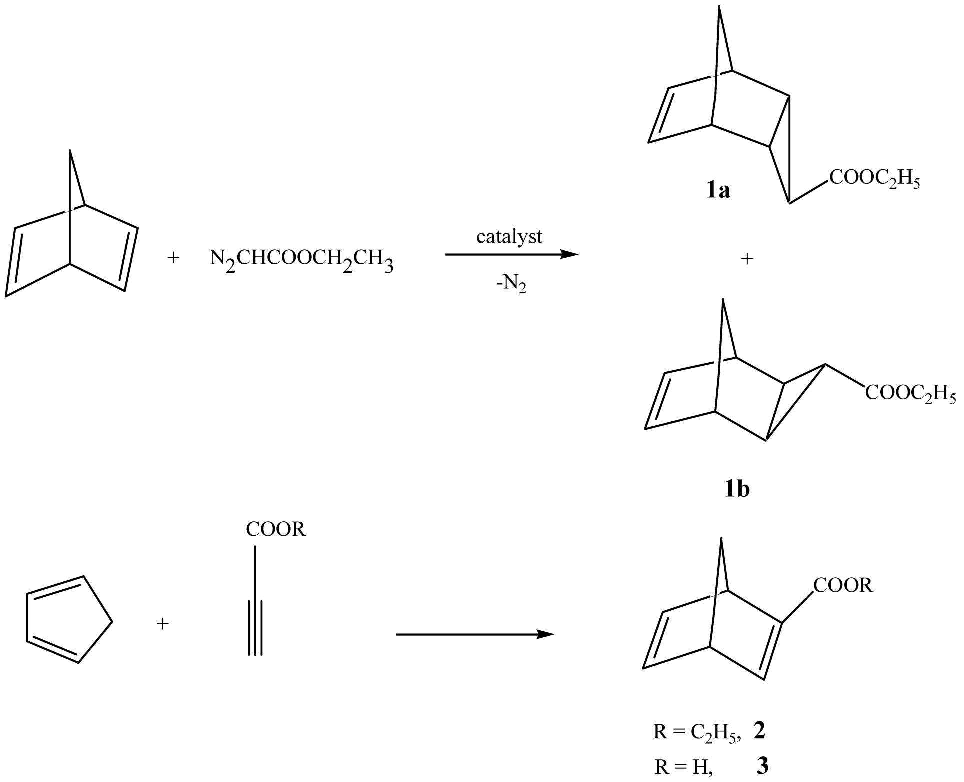
3.1. Synthesis and characterization of monomers

Monomer **1** was obtained from norbornadiene via addition of ethoxycarbonyl prepared from ethyl diazoacetate (EDA) (Scheme 1). The cyclopropanation of alkenes with EDA is efficiently catalyzed by several transition metals and their complexes [12,14,15]. Our interest in the synthesis of polycyclic compound **1** in good yield prompted us to optimize the cyclopropanation reaction and to separate the pure compound. Therefore, the cyclopropanations were carried out by treating the norbornadiene with EDA in the presence of different types of catalysts. The results of the cyclopropanation reaction are summarized in Table 1. The maximum yield (ca. 56%) was obtained in the CuCN catalysed reaction. Relatively pure monomer **1** was obtained in this case after two consecutives vacuum distillations. NMR analysis confirmed a mixture of *syn-endo* **1a** and *anti-exo* **1b** adducts, in a ratio of about 1/2.3. Reactions catalyzed by Rh(II) and Pd(II) carboxylates (Table 1, run 1–2) yielded quantitatively a mixture of monomer **1** and diethyl fumarate/diethyl maleate.

Monomers **2** and **3** were prepared by standard Diels–Alder addition of cyclopentadiene to acetylene derivatives (Scheme 1). Monomers **1** and **2** were clear liquids while **3** was colorless crystals with a melting point of 78 °C. The spectral data of all compounds were in agreement with the expected structure (see Section 2).

3.2. Polymerization of monomers

Monomers of the norbornadiene type **1**–**3** undergo free radical polymerization in bulk and in solution (Scheme 2). The bulk polymerizations involved initiation with BP at 80 °C or spontaneous initiation on standing in air. The



Scheme 1. Synthesis of monomers **1**–**3**.

solution polymerizations of monomers **1** and **2** initiated with AIBN at 65 °C were homogeneous, while the polymer resulting from the monomer **3** precipitated from the solution, leading to a heterogeneous system. The resulting polymers were powder, colorless to yellow, with different solubility (Table 2). Poly-**3** was less soluble than the others, possibly due to polymer chain interactions, e.g. hydrogen bonding.

The polymers were investigated by gel permeation chromatography. Generally, the presence of solvent reduces the yield and the molecular weight of the polymer. Table 3 summarizes the experiments performed and the characterization of the resulting polymers.

Monomer **1**, the tricyclic derivative, showed a poor reactivity either in a bulk polymerization for 20 h or in a solution polymerization for 22 h. The polymerization initiated with AIBN at 65 °C gave only traces of polymer poly-**1** (Table 3, run 2) and the use of BP as initiator at elevated temperature (80 °C) resulted in an increased yield.

Monomer **2** underwent high conversion to a partially soluble polymer when polymerized in bulk, but a completely soluble polymer was obtained from THF or benzene solution. This is probably due to the high molecular weights obtained in bulk polymerization or some crosslinking may take place during polymerization. In this case, the GPC data are reported for soluble fraction extracted by stirring 6 h (Table 3, run 4). Upon extended storage at room temperature monomer **2** slowly polymerized spontaneously, a conversion of about 50% being achieved after 24 h (Table 3, run 6).

Monomer **3** readily polymerized with free radical initiators in THF or benzene solution to high conversions. The obtained polymer is insoluble in typical organic solvents but it is quite soluble in aqueous NaOH solution.

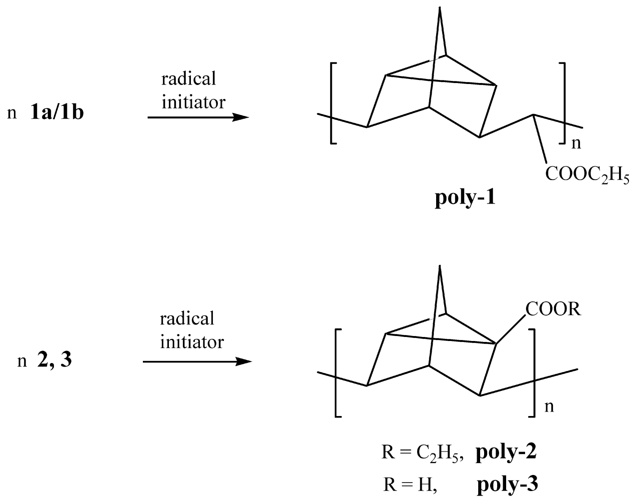
Table 1
Reaction conditions for the synthesis of monomers **1**–**3**

Run	Monomer	Catalyst	Solvent	Temperature (°C)	Description	Yield (%)
1	**1**[a]	$Pd(OAc)_2$	With/without hexane	60	Colorless liquid	35
2		$Rh(OAc)_2$	With/without hexane	60	Colorless liquid	28
3		CuCN	With/without hexane	60	Colorless liquid	56
4	**2**[b]	No catalyst	Benzene	60	Colorless liquid	60
5	**3**[c]	No catalyst	Chloroform	55	Colorless solid	36

[a] Molar ratio norbornadiene/EDA = 1.2/1; molar ratio catalyst/EDA = 0.05/1, 60 °C, 3.5 h.

[b] Molar ratio cyclopentadiene/ethyl propiolate = 1.3/1, 60 °C, 24 h.

[c] Molar ratio cyclopentadiene/propiolic acid = 4/1; 55 °C, 3 h.



Scheme 2. Polymerization reactions of monomers **1**–**3**.

This suggests a polyelectrolyte character of the obtained free-acid polymer. The polymer produced from bulk polymerization resulted in a product that is only partially soluble in H_2O/NaOH and swells in DMSO.

3.3. Spectroscopic analyses

The structural characteristics of polymer poly-**1** were obtained from IR and NMR measurements. No residual stretch vibration at 1545 cm^{-1} corresponding to double bond of the monomer could be detected in FTIR spectrum of product poly-**1**. As a consequence of the polymerization process, the characteristic signal of the carboxylic ester group at 1726 cm^{-1} from the monomer is significantly shifted to a lower wavenumber of 1715 cm^{-1} after polymerization. The ^{1}H NMR spectrum of the polymer indicates the absence of unsaturation and are devoid of absorption in the region below 7 ppm. Due to the broad signals in ^{1}H NMR spectrum of polymer poly-**1** it is not possible to make a definitive conclusion about the exact unit structure in the polymer chain. To obtain more information regarding assignment of the polymer, ^{13}C and DEPT NMR spectroscopy were measured and these spectra are presented in Fig. 1. Comprehensive ^{13}C NMR studies on a number of norbornene derivatives have been published [16–19]. The vinyl resonances of the monomer at 142.3 and 132.1 ppm (carbons D and d, respectively) disappear in the polymer spectrum and the signals of the formed methine groups (carbons 4 and 4′) appear upfield (16.8 and 22.0 ppm). The presence of two different signals for methine group (carbons 2 and 2′) at 22.3 and 25.2 ppm, respectively, coupled with the shifting of the signal corresponding to the carbons e, E from 14.6 to 25.2 ppm (carbon 5) were indicative for the opening of cyclopropyl ring and the existence of the nortricyclene structure in the polymer. More specialized ^{1}H NMR measurements (1D- and 2D-COSY, HMBC and TOCSY) confirmed the mechanism proposed in Scheme 3.

The formation of nortricyclene unit occurs by the radical addition to the double bond, followed by the formation of a new cycle concomitant with the opening of cyclopropane ring which is held in the close proximity. A carbon-centered radical intermediate is formed and continues the chain propagation by reacting with another molecule of monomer (Scheme 3). Theoretical calculations on intramolecular ring-closing processes by Gravel et al. [20] have shown that cyclopropanation is a favorable process in activated norbornadiene structures. On the other hand, Sanda showed that the vinyl group which is in the proximity of a cyclopropyl ring affords ring-opening polymerization [21].

By analogy with free-radical reactions of bicyclo[2.2.1]-hepta-2,5-diene [22] the polymerization of monomers **2** and **3** involve a cyclization process (Scheme 2). The ^{1}H NMR spectra for the polymers poly-**2** and poly-**3** show that their structures are similar to those of a polymer sample previously reported by Graham [8] and Frechet [10].

3.4. Kinetic study

Concerning the possibility to use these monomers for materials with dental applications, it was of interest to compare the overall polymerization behavior of norbornadiene derivatives **1**–**3** with methyl methacrylate. The reactivity of these monomers in radical polymerization was studied by determination of residual monomer concentration during polymerization by use of UV measurements. Fig. 2 presents the kinetic curves obtained for the solution polymerization of monomers **1**–**3** in comparison with MMA. All monomers were polymerized in THF, with AIBN at 65 °C in the case of MMA and monomers **2** and **3**, and with BP at 80 °C, in the case of monomer **1**. THF is known as a solvent with high chain transfer constant. In order to have comparable kinetic data,

Table 2
Solubility data

Polymer	Solvent							
	$CHCl_3$	CH_2Cl_2	DMSO	DMF	Acetone	THF	Benzene	NaOH/H_2O
Poly-**1**	++	++	++	+	+	+	++	−
Poly-**2**	++	++	+	++	~	++	++	−
Poly-**3**	−	−	o	o	−	−	−	++

++: Soluble at room temperature, +: soluble on heating at 70 °C, −: insoluble, ~: partially soluble, o: swollen.

Table 3
Polymerization data of monomers **1**–**3** (BP: benzoyl peroxide, AIBN: 2,2′-azoisobutyronitrile)

Run	Monomer	Initiation	Solvent	Time (h)	Temperature (°C)	Conversion (%)	M_w[a]	M_n[a]	PDI
1	**1**	BP	Bulk	20	80	25	3700	2600	1.42
2	**1**	AIBN	C_6H_6	22	65	Traces	–	–	–
3	**1**	BP	C_6H_6	22	80	22	1820	1600	1.13
4	**2**	BP	Bulk	20	80	73	103 400[b]	22 600[b]	4.57[b]
5	**2**	AIBN	C_6H_6	22	65	61	37 000	19 600	1.88
6	**2**	–	–	24	Room temperature	50	44 300	21 200	2.10
7	**3**	BP	Bulk	2	90	92	–	–	–
8	**3**	AIBN	C_6H_6	6	65	66	5800[b]	3100[b]	1.87[b]

[BP] = 5 mol%. [Monomer] = 50 wt%, [AIBN] = 2 mol%.

[a] Determined by gel permeation chromatography.

[b] Determined for soluble fraction.

good solubility of monomers and polymers in selected solvent is required. As it was mentioned before, poly-**3** is insoluble in THF but the polymerization takes place in homogeneous solution during the first 90 min, after which the polymer starts to precipite. This is likely due to increasing of polymer concentration when the interactions between macromolecular chains become stronger. Thus, after this time, the conversion was determined gravimetrically.

The conversion-time plots show that tendency of polymerization decrease in the order: MMA > **3** > **2** > **1**.

It is known that a rapid polymerization requires low sterical hindrance, an electron-withdrawing substituent to activate one of the double bonds and provide resonance stabilization of radicals formed during the polymerization. In our case, the higher reactivity of compound **3** is due to the easier accessibility of the initiator radicals to the activated double bond. This is in accordance with the higher slope of the kinetic plot in the initiation step for the polymerization of monomer **3** as compared with monomer **2**. Introduction of a cyclopropyl ring could be expected to afford even more rapid polymerization, apparently due to the ring strain and steric effects. However, due to the existence of an inactivated double bond, compound **1** is relatively stable and the cleavage of the σ bond of the cyclopropane ring requires intense reaction conditions (i.e. high temperatures, long reaction time). A detailed kinetic study on radical homo- and copolymerization of monomer **1** is under progress and will be published at a later date.

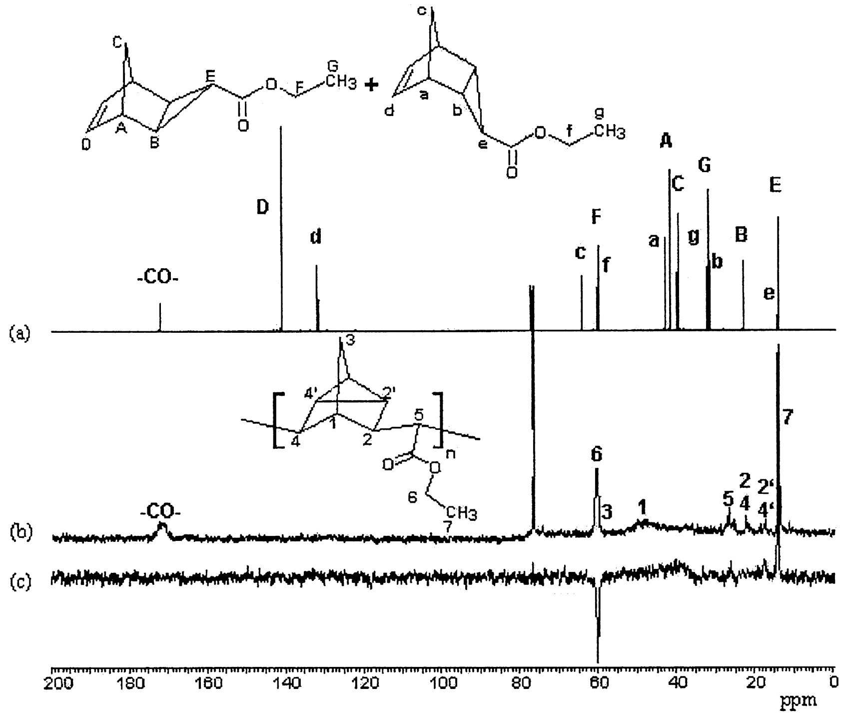
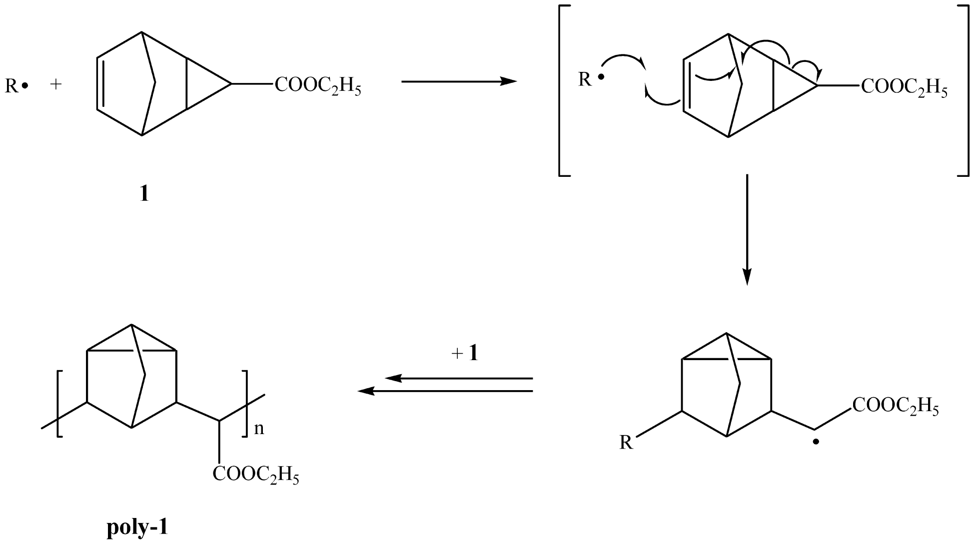


Fig. 1. ^{13}C NMR spectra of (a) monomer **1** and (b) polymer poly-**1** and (c) DEPT NMR spectrum of poly-**1** in $CDCl_3$ at room temperature.



Scheme 3. Proposed mechanism for the free-radical polymerization of monomer **1**.

4. Conclusions

It has been shown that 3-ethoxycarbonyl-tricyclo[3.2.1.0^{2,4}]oct-6-ene can be converted, in the presence of radical initiators, in a stable polymer with nortricyclene repeating backbone units. Instead of normal vinyl polymerization, the free-radical mechanism involves an intramolecular cyclopropanation accompanied by a ring-opening process, as NMR measurements indicated. The comparative kinetic study on polymerization of this monomer and another two norbornadiene derivatives evidenced its poor reactivity in radical homopolymerization. Polynortricyclene structure opens a perspective to use these materials in optical applications but the low reactivity in comparison with MMA make these monomers rather restricted suitable for medical applications.

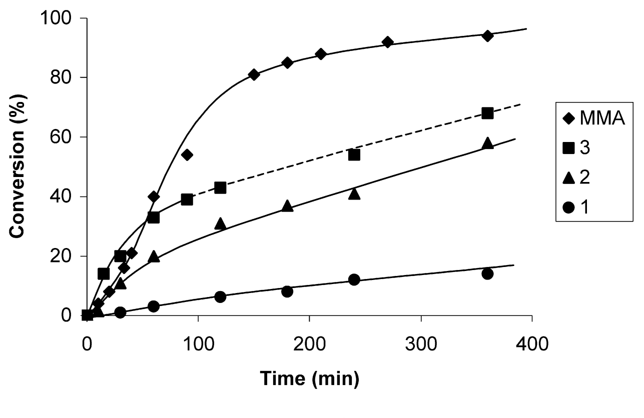


Fig. 2. Conversion versus time plots for the solution polymerization of monomers **1**–**3** (reaction conditions: **1**—THF, 5 mol% BP, 80 °C, 22 h; **2**, **3**, **MMA**—THF, 2 mol% AIBN, 65 °C, 22 h; AIBN: 2,2′-azoisobutyronitrile, BP: benzoyl peroxide).

Acknowledgements

Financial Support by EC Project ‘DENTALOPT’ (G5RD-CT2001-00554) is gratefully acknowledged.

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