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Living Radical Polymerization of Bicyclic Dienes: Synthesis of Thermally Cross-Linkable Block Copolymers

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ABSTRACT: A new thermal cross-linking strategy based on retro-Diels–Alder reaction of bicyclic diene polymers was developed. 2,3-Dimethylenenorbornane (**1**) and its derivatives polymerized under free-radical conditions predominantly via the 1,4-addition mode. Monomer **1** had a much higher reactivity toward propagating polymer radicals than isoprene despite having larger substituents, which was attributed to the rigid *s-cis* coplanar conformation of the diene group in **1**. Nitroxide-mediated polymerization at 110 °C provided bicyclic diene polymers with controlled molecular weights and narrow molecular weight distributions, as well as block copolymers of **1** and methyl acrylate. Poly(**1**) underwent retro-Diels–Alder reaction with a concurrent release of ethylene upon heating at 245 °C, which ultimately led to the formation of cross-linked structures. Block copolymers of **1** and methyl acrylate phase-separated into lamellae and cylindrical microstructures when annealed at 180 °C. Upon further heating to 245 °C, the poly(**1**) domain in the block copolymer cross-linked to provide rigid polymer nanostructures, which was monitored by a gradual increase in its glass transition temperature. The morphology formed by block copolymer phase separation was preserved during the cross-linking process, as confirmed by a small-angle X-ray scattering analysis.

Introduction

Self-assembly of block copolymers provides an access to nanostructured soft materials. Amphiphilic block copolymers can form spherical, cylindrical, or wormlike micelles and vesicles in selective solvents, such as water.[1,2] In the solid state, phase separation of block copolymers leads to a variety of microstructures depending on the strength of interactions between the blocks and their corresponding volume fractions.[3−5] A broad spectrum of formed morphologies opens up a variety of possibilities for the utilization of these materials in drug delivery, ultrafiltration, and high-density magnetic storage, to name a few. In some applications, the dynamic nature of block copolymer self-assembly plays a crucial role in obtaining stimuli-responsive materials, while in other applications, it is desirable to fix (cross-link) the prepared microstructures to provide robust and rigid frameworks for prolonged durability and further modifications. For example, shell-cross-linked and core-cross-linked block copolymer micelles have gained an increasing interest for drug delivery applications, where fixation of self-assembled polymer micelles provides more robust spherical nanoparticles.[6−12] Cross-linked cylindrical microstructures obtained from block copolymers in thin films and melt provide an access to versatile, solvent- and temperature-resistant nanoporous templates.[13,14] Phase-separated block copolymer microstructures can also be used to fabricate nanofibers and nanotubes by cross-linking the minority component.[15−17] Intramolecular cross-linking of low-polydispersity polymers and block copolymers in dilute solutions has been used to prepare well-defined organic nanoparticles.[18,19]

A variety of different cross-linking strategies have been utilized so far, including chemical reactions with difunctional reagents and photochemical fixation. The simplest possible trigger, temperature, has been scarcely used to initiate cross-linking of block copolymer systems, mainly due to the lack of thermosensitive monomers that satisfy a multitude of requirements posed by the complexity of block copolymer synthesis and self-assembly protocols. Successful monomers should be amenable to living polymerizations protocols, be stable at polymerization temperature, have the cross-linking temperature (T_{cr}) higher than the glass transition temperature (T_{g}) and below the decomposition temperature (T_{d}), and also undergo cross-linking without significant weight loss. Recently, Hawker et al. introduced a new styrenic monomer containing a benzocyclobutane functionality that can dimerize, and therefore lead to cross-linking, when heated above 220 °C.[18] While benzocyclobutane chemistry has been known for years,[20−23] vinylbenzocyclobutane developed by Hawker and co-workers can be polymerized by living radical polymerization methods and can be therefore incorporated into well-defined polymers and block copolymers. A variety of interesting materials have been prepared on its basis, including robust nanoporous templates[13] and well-defined organic nanoparticles.[18]

Diels–Alder chemistry has also been extensively explored for the preparation of thermally reversible polymer networks. After a pioneering work on cyclopentadiene containing polymers by Kennedy et al.,[24] a variety of other thermally cross-linkable polymers have been introduced, mainly based on cyclopentadiene dimerization[25,26] and furan-maleimide cycloaddition.[27−29] Shape memory polymers and thermally remendable epoxy resins are a couple of recent examples of the utilization of this chemistry for the preparation of advanced materials.[30−32]

The availability of synthetically accessible and versatile thermosensitive monomers that are amenable to living radical polymerization protocols will open new avenues for the utilization of thermocurable block copolymer nanostructures. In this article, we report a living polymerization of easily accessible bicyclic diene monomers. The obtained polymers are stable and can be easily processed. Above certain temperature,

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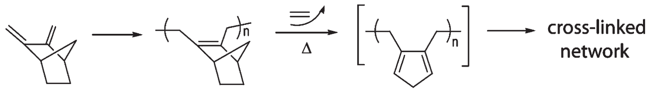
Scheme 1



they undergo retro-Diels–Alder reaction with a concurrent ethylene release and a subsequent self-cross-linking (Scheme 1). We also demonstrate that phase-separated block copolymer microstructures can be successfully cured using this methodology.

Experimental Section

Materials. Methyl acrylate (MA) and isoprene were purified by distilling from CaH_2. All chemicals were used without further purification unless stated otherwise. 2,3-Dimethylenebicyclo[2.2.1]-heptane (**1**),[33] 2,3-bis-exomethylene-1,4-methano-1,2,3,4-tetrahydroanthracene (**2**),[34] 2,3-dimethylene-7-oxabicyclo[2.2.1]heptane (**3**),[35] and 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TMPEPA)[36] were synthesized according to literature procedures.

Copolymers of 1 and Isoprene. A mixture of monomer **1**, isoprene, and AIBN was degassed by three freeze–pump–thaw cycles, sealed under nitrogen, and placed in an oil bath at 60 °C. After 2 h, the contents were diluted with dichloromethane and precipitated in methanol. The molar ratios of monomer **1** and isoprene were set to 1:9, 2:8, 7:13, 1:1, 13:7, and 8:2, and the concentration of AIBN was maintained at 1 wt %. The polymer composition was determined by ^{1}H NMR. Reactivity ratios were calculated by a nonlinear curve fitting method.

General Procedure for Nitroxide-Mediated Polymerization. A mixture containing a monomer (0.2–0.5 mL), TMPEPA, and toluene (only for **2**) was degassed by three freeze–pump–thaw cycles, sealed under nitrogen, and placed in an oil bath at 110 °C. After certain time, the contents were diluted with dichloromethane and precipitated in methanol or ether. The polymer was filtered and dried in a vacuum oven overnight.

Poly(MA-*b*-1). A mixture of TMPEPA (3.0 mg, 9.2 μmol), the corresponding nitroxide free radical (1.0 mg, 4.5 μmol), and MA (170 mg, 2.0 mmol) was degassed by three cycles of freeze–pump–thaw, sealed, and placed in an oil bath at 125 °C for 20 h. The viscous reaction mixture was then dissolved in dichloromethane and precipitated in methanol. The polymer was filtered and dried in a vacuum oven overnight. Yield = 90 mg. GPC (light scattering detector): $M_n = 8.2$ kg/mol, $M_w/M_n = 1.12$. Poly(MA), the starting block (50 mg, 1.9 μmol), was then redissolved in a mixture of monomer **1** (0.5 g, 4.2 mmol) and toluene (0.3 mL). Acetic anhydride (1 mg, 10 μmol) was then added, and the polymerization reaction mixture was heated at 125 °C for 6 h. The contents were diluted with dichloromethane and precipitated in methanol. The product was filtered and dried in a vacuum oven. Yield = 0.12 g. GPC (polystyrene standards): $M_n = 34.5$ kg/mol, $M_w/M_n = 1.36$.

Measurements. GPC analysis was carried out on Viscotek's GPCMax with two PolyPore columns (Polymer Laboratories, Varian Inc.) and TDA302 tetradetector array system which contained refractive index, UV, viscosity, and low (7°) and right angle light scattering modules. THF was used as a carrier solvent at 30 °C. The system was calibrated with 10 polystyrene standards from 1.2×10^6 to 500 g/mol. Refractive index increments (d*n*/d*c*) for poly(**1**) and poly(MA) were measured to be 0.131 and 0.056 mL/g in THF ($T = 30$ °C, $\lambda = 630$ nm), respectively, and were used to determine absolute molecular weights of the homopolymers. NMR measurements were performed on a Varian Inova-500 (500 MHz) spectrometer by using $CDCl_3$ as a solvent. Differential scanning calorimetry (DSC) was conducted on a TA Instruments Q200 system with an RCS-90 cooling device. Glass transition temperatures were measured on a second heating scan at a rate of 10 °C/min. Small-angle X-ray scattering studies were carried out by using a Bruker Nanostar system with 2D area detector. Thermal gravimetric analysis was performed on a Perkin-Elmer TGA7 under nitrogen flow at 10 °C/min heating rate. UV–vis spectra of monomers were obtained on Agilent 8453 at room temperature by using hexane as a solvent.

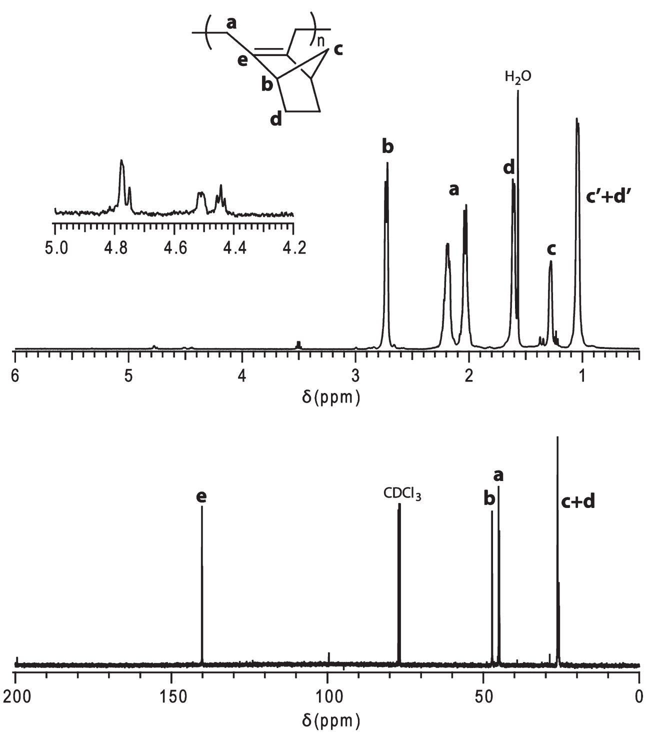
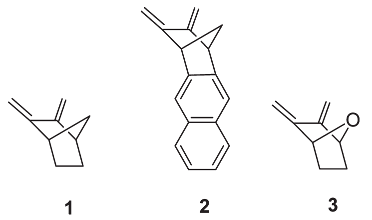


Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of poly(**1**) in $CDCl_3$.

Scheme 2



Results and Discussion

Monomer Synthesis. We prepared three different monomers with norbornane skeletons containing exo diene groups (Scheme 2). Monomer **1**, which is the main focus of this report, was synthesized in three steps: via Diels–Alder addition of cyclopentadiene and 1,4-dichloro-2-butene, catalytic hydrogenation, and a subsequent dehydrohalogenation.[33] The product was prepared on a 10 g scale and was purified by distillation. The synthesis provided a good yield and was readily amenable to scale-up. Monomers **2** and **3** were also prepared according to the literature procedures in multigram quantities.[34,35]

Radical Polymerization. Emulsion polymerization of **1**, carried out by Wood et al. in 1960,[33] was reported to proceed exclusively via 1,4-addition, as characterized by infrared spectroscopy. We first conducted free-radical polymerization of **1** in a neat monomer at 60 °C with AIBN as the initiator. The polymer was characterized by ^{1}H and ^{13}C NMR, which confirmed a predominant 1,4-addition mode during polymerization (Figure 1). Bridgehead protons (**b**) had a chemical shift of 2.75 ppm, backbone methylene groups (**a**) appeared in the range of 2–2.3 ppm, while two bridge protons (**c**) had chemical shifts of 1.3 and 1.05 ppm, overlapping with the signal from ring methylene groups (**d**). In the ^{13}C NMR spectrum, quaternary olefin carbons (**e**) had a distinctive chemical shift of 140 ppm. In the ^{1}H NMR spectrum, we also observed small peaks at around 4.8 and 4.5 ppm region, which were attributed to vinyl protons of the 1,2-adduct. The chemical shifts of these signals were similar to those observed in the ^{1}H NMR spectrum of (commercially available) camphene (Supporting Information, Figure S1), which is a small molecule mimic of the 1,2-adduct. From signal intensities, it appears that less than 5% of repeat units came from 1,2-addition. Both monomers **2** and **3** also polymerized predominantly by 1,4-addition (Supporting Information, Figures S2 and S3). However, in the ^{1}H NMR spectrum of poly(**3**), we observed some peaks (4.25, 4.50–4.75 ppm) that could not be attributed to either 1,4- or 1,2-addition product and perhaps are the result of an unknown side reaction during propagation. From NMR signal intensities it appears that ~80% of repeat units in poly(**3**) are originating from the expected 1,4-addition.

The polymerization of **1** appeared to be noticeably faster than that of isoprene, which is less sterically crowded than **1**. We measured initial rates of polymerization for both monomers at 60 °C and calculated their $k_p/\sqrt{k_t}$ values using the reported $k_d = 9.03 \times 10^{-6}$ s^{-1} for AIBN[37] and assuming initiation efficiency $f = 0.5$, where k_p, k_t, and k_d are rate constants for propagation, termination, and initiator decomposition, respectively. The ratio between the rate constant of propagation and a square root of the rate constant of termination is often referred to as polymerizability and measures the propensity of a certain monomer to polymerize. The calculated $k_p/\sqrt{k_t}$ values for monomer **1** and isoprene were 1.07×10^{-2} and 4.7×10^{-3} L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$, respectively, indicating that this bicyclic diene polymerizes 2.3 times faster than isoprene despite the presence of bulkier substituents and a strained ring in monomer **1**.

We also conducted copolymerizations of isoprene and monomer **1** at 60 °C at six different monomer feed compositions in order to determine monomer reactivity ratios. Using a nonlinear curve fitting method, we calculated reactivity ratios r_1 and r_2 to be 3.17 and 0.65, respectively, where M_1 was monomer **1** and M_2 was isoprene (Supporting Information, Figure S4). The obtained results suggest that both polyisoprene and poly(**1**) propagating radicals add much faster to monomer **1** than to isoprene, confirming the enhanced reactivity of **1**.

Such a high reactivity of monomer **1** was attributed to its rigid conformation where two double bonds are fixed in the *s-cis* coplanar arrangement, thus increasing the conjugation character of the diene. Characterization of **1** by UV–vis spectroscopy revealed a $\lambda_{max} = 247$ nm, as compared to isoprene's $\lambda_{max} = 223$ nm. Longer absorption wavelength for **1** was consistent with other cyclic dienes with *s-cis* conformations, such as 1,2-dimethylenecyclopentane.[38] When the two double bonds in a cyclic diene are forced out of a coplanar arrangement, e.g., in 1,2-dimethylenecyclohexane, the absorption maximum shifts to shorter wavelengths,[38] and the polymerizability of the monomer drastically decreases.[39] Thus, there is a strong correlation between the conformation of a diene molecule and its reactivity, which results in much faster polymerization rates for **1** as compared to isoprene, even though monomer **1** contains bulkier and strained substituents.

Controlled Polymerization. Living radical polymerization of monomers **1**–**3** was carried out with a universal nitroxide initiator, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TMPEPA),[36] as this was one of a few documented methods for controlled polymerization of dienes, such as butadiene and isoprene.[40–43] When polymerizations were conducted at a typical for isoprene $T = 125$ °C, only polymers with broad molecular weight distributions could be obtained. However, at a lower temperature of 110 °C, we were able to produce polymers with low polydispersities for all three monomers (Table 1). This behavior can be attributed to two factors: (i) higher reactivity of bicyclic monomers **1**–**3**, compared to isoprene, and (ii) increased steric hindrace that could lead to easier dissociation of the nitroxide bond in the dormant chain ends of bicyclic diene polymers.

Table 1. Nitroxide-Mediated Polymerization of Bicyclic Dienes[a]

monomer	time (h)	conversion (%)	M_n (kg/mol)[b]	M_w/M_n[b]
1	28	68	8.7 (17.3)	1.18
1[c]	19	67	7.9 (13.5)	1.40
2[d]	10	70	19.6	1.20
3	26	72	11.5	1.10

[a] $T = 110$ °C, neat monomer; TMPEPA was used as the initiator; [M]:[TMPEPA] = 150:1. [b] Measured by SEC with polystyrene calibration. The numbers in parentheses were obtained from SEC with a light scattering detector. [c] $T = 125$ °C. [d] Conducted in 50 wt % toluene solution.

A detailed kinetic analysis of the nitroxide-mediated polymerization of monomer **1** was carried out at 110 °C. Absolute molecular weights of the prepared polymers were obtained by SEC with a light scattering detector. After an initial jump, the polymer molecular weight increased linearly with conversion, while polydispersities remained narrow (Figure 2). In the first-order kinetic plot, a linear behavior was observed in the beginning, while at longer reaction times, the polymerization slowed down (Figure 2). These kinetic features can be attributed to the generation of a high radical concentration in the initial stages of the polymerization, which leads to a buildup of nitroxide radicals and subsequent controlled polymerization. It is possible that the nitroxide dissociation from the dormant polymer chains is too rapid even at 110 °C due to steric hindrance of poly(**1**) radical. The use of lower temperatures, however, was not possible due to the fact that the nitroxide initiator TMPEPA cannot dissociate rapidly at lower temperatures. Despite these limitations, polymers with narrow molecular weight distributions and controlled molecular weights could be prepared under the studied conditions.

Block copolymers of **1** and methyl acrylate (MA) were synthesized by the sequential polymerization of each monomer (Scheme 3). Poly(MA) macroinitiator was prepared first by using conditions reported by Hawker et al.,[36] followed by the synthesis of poly(**1**) at 125 °C as the second block. SEC analysis confirmed efficient reinitiation and the formation of well-defined block copolymers (Figure 3). It was important to grow poly(MA) block first. When copolymer synthesis was conducted the other way around, i.e., poly(**1**) was prepared first and poly(MA) second, block polymers with bimodal molecular weight distributions were obtained, indicating inefficient initiation. Table 2 summarizes structural characteristics of the prepared block copolymers.

Glass Transition. Glass transition temperatures (T_g) of poly(**1**), poly(**2**), and poly(**3**) were determined by differential scanning calorimetry (DSC) to be 35, 203, and 106 °C, respectively. These values were obtained for high molecular weight polymers prepared by living radical polymerization (Table 1). Consistent with its very bulky and rigid aromatic substituent, poly(**2**) has the largest T_g. On the other hand, the T_g value of poly(**1**) appears to be too low for a polymer bearing bicyclic groups in the backbone. The chemical structure of the repeat unit of poly(**1**) is very similar to that

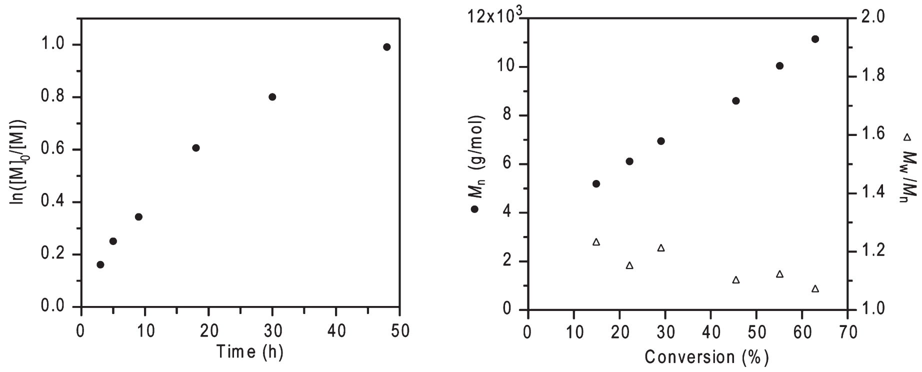
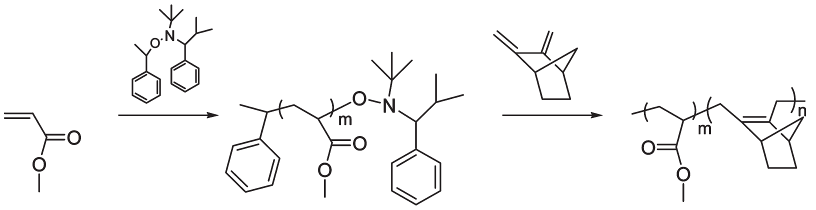


Figure 2. First-order kinetic plot (left) and molecular weight dependence on conversion (right) for nitroxide-mediated polymerization of **1** at 110 °C ([**1**]$_0$:[TMPEPA]$_0$ = 200:1).

Scheme 3



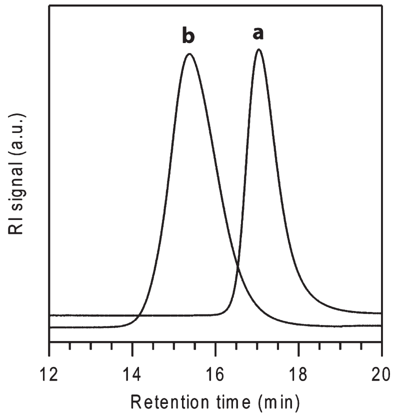


Figure 3. SEC analysis of (a) poly(MA) macroinitiator and (b) poly(MA)−poly(**1**) block copolymer.

Scheme 4

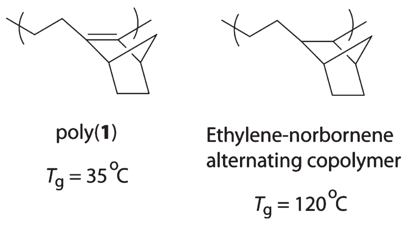


Table 2. Synthesis of Poly(MA)−Poly(1) Block Copolymers[a]

block copolymer	time (h)	M_n (kg/mol)[b]	M_w/M_n[b]	PMA (wt %)[c]	morph[d]
BDA-1	4	22.9	1.36	36	L
BDA-2	9	34.5	1.38	24	C

[a] T = 125 °C; PMA (M_n = 8.2 kg/mol, M_w/M_n = 1.12) was used as the initiator. [b] Measured by GPC with polystyrene calibration. [c] Calculated from NMR data. [d] Morphology as identified by SAXS analysis at 25 °C, L: lamellae; C: cylindrical.

of an alternating ethylene−norbornene copolymer that can be prepared by coordination polymerization (Scheme 4). The only difference is the presence of unsaturations in the poly(**1**) backbone. Glass transitions temperatures reported for poly(ethylene-*alt*-norbornene) copolymers[44] and of random ethylene−norbornene copolymers[45] with an equimolar composition are in the range of 120−140 °C, substantially higher than T_g of poly(**1**). To investigate the effect of unsaturations on the glass transition temperature, we prepared a fully hydrogenated poly(**1**), which is a chemical equivalent of an alternating ethylene−norbornene copolymer. While hydrogenation of poly(**1**) by Pd/C catalyst under up to 1000 psi of hydrogen pressure proved to be ineffective, we were able to generate a fully hydrogenated poly(**1**) by using diimide chemistry. ^{1}H NMR of the hydrogenated polymer showed complete disappearance of unsaturations, as signals corresponding to bridgehead and backbone methylene groups moved upfield (Supporting Information, Figure S5). DSC analysis of the hydrogenated poly(**1**) revealed a T_g of 105 °C, which was close to the glass transition temperatures reported for alternating ethylene−norbornene copolymers and was significantly higher than that of the unhydrogenated, pristine poly(**1**). Such a large difference in T_g values between hydrogenated and unhydrogenated poly(**1**) confirmed a dramatic effect of the double bond on the polymer backbone flexibility. This effect is perhaps unique to polymers with bicyclic groups and is related to the relative orientation of substituents on a norbornane ring.

The difference in T_g values of poly(**1**) and poly(**3**) is also quite substantial (ΔT_g = 71 °C) given that they are structurally nearly identical and only differ by one atom. In other similar cases, where polymers differ only by one atom, e.g. poly(ethylethylene) vs poly(methyl vinyl ether), no significant difference in T_g values could be observed.[37] In the case of poly(**3**), such an unusual increase in T_g could perhaps be attributed to the increased dipole moment of the repeat unit in poly(**3**) relative to poly(**1**). It is also possible that the side reaction present during propagation of **3** (vide supra) might lead to the presence of very rigid repeat units in the backbone. It must noted that T_g values for poly(**1**) and poly(**3**) are

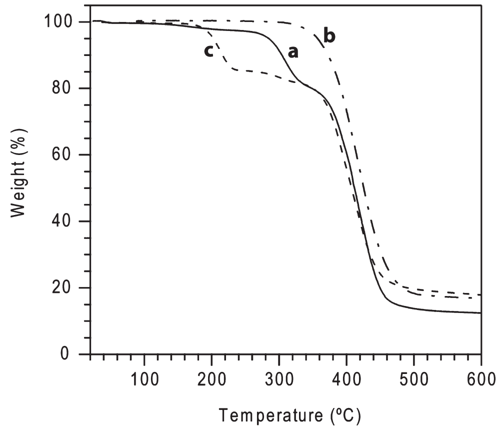


Figure 4. TGA curves for (a) poly(**1**), (b) poly(**2**), and (c) poly(**3**).

in close agreement with softening points reported by Woods et al., for the polymers prepared by emulsion polymerization.[33]

Thermogravimetric Analysis. All three polymers decomposed upon heating to 360 °C. Poly(**1**) and poly(**3**) exhibited a separate weight loss step prior to degradation (Figure 4), which was attributed to retro-Diels–Alder reaction taking place with a concurrent release of ethylene (Scheme 1). The weight of loss of ~20% was observed for both polymers, in good agreement with the weight percent of ethylene in polymer repeat units. The onset transition temperatures (T_{DA}) for poly(**1**) and poly(**3**) were 280 and 180 °C, respectively. A much lower transition temperature for poly(**3**) is driven by the formation of aromatic furan rings as the product, while the absence of such transition in poly(**2**) is consistent with its inability to undergo cycloreversion.

Polymers of **1** and **3** were heated above T_{DA} but below their decomposition temperatures and then cooled to room temperature. The product of such thermal treatment of poly(**3**) was soluble in common organic solvents and thus could be analyzed by ^{1}H NMR. A new strong signal at 7.2 ppm was observed in the NMR spectrum, confirming the formation of furan rings (Supporting Information, Figure S2). On the other hand, the product of thermal treatment of poly(**1**) was completely insoluble in organic solvents, suggesting the formation of cross-linked structures. We attributed this behavior to the dimerization of cyclopentadiene groups formed as a result of retro-Diels–Alder reaction of poly(**1**).[24–26] We also carried out the thermal treatment of poly(**1**) under vacuum, since retro-Diels–Alder reaction can be driven by removing ethylene side product. Under these conditions, poly(**1**) could be cross-linked at temperatures as low as 245 °C.

Cross-Linked Nanostructures. Thermal cross-linking of poly(**1**) was exploited for the fixation of nanostructures formed by the block copolymer phase separation. Block copolymers of **1** and methyl acrylate (vide supra) were annealed at 180 °C for 24 h. At this temperature, polymers were stable and did not undergo cross-linking, which was confirmed by GPC analysis. Annealed block copolymer samples were then analyzed by small-angle X-ray scattering (SAXS) at room temperature. Both polymers showed a strong primary scattering peak and several higher order reflections, which confirmed microphase separation and allowed us to determine the symmetry of formed morphologies (Table 2).

Block copolymer BDA-2, with a cylindrical morphology, was then heated in a vacuum oven at 245 °C in order to promote retro-Diels–Alder reaction and subsequent cross-linking. We followed the kinetics of ethylene release by running TGA on polymer samples annealed at 245 °C for a certain number of hours. Unreacted repeat units release ethylene during thermogravimetric analysis, which allows for the quantitative characterization of retro-Diels–Alder reaction taking place during the preceding thermal treatment. A first-order kinetic plot of ethylene release (Figure 5) shows linear behavior initially before concaving down at longer reaction times. We attribute the deviation from linearity at higher conversions to the formation of rigid structures upon cross-linking and a corresponding slower ethylene diffusion through the sample. This is an example of a self-inhibiting reaction. Enough ethylene is released to obtain a rigid network, which subsequently slows down further ethylene escape and eventually stop the reaction completely.

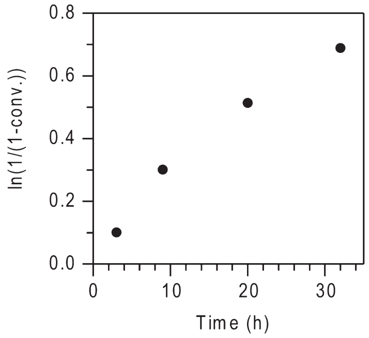


Figure 5. First-order kinetic plot for ethylene release from BDA-2 block copolymer at 245 °C.

Concurrently, we used DSC to monitor the formation of a cross-linked network during the thermal treatment. Figure 6 depicts DSC curves for the block copolymer BDA-2 annealed at 245 °C. The original curve (t = 0 h) shows two glass transitions at 35 and 18 °C, corresponding to poly(**1**) and poly(MA) blocks in the copolymer, respectively. The presence of two separate T_g suggests phase separation, which is in agreement with SAXS results. After annealing at 245 °C, T_g corresponding to poly(**1**) block slowly increases, and after 32 h, no T_g could be observed. On the other hand, T_g corresponding to poly(methyl acrylate) block remains constant at 18–20 °C. These results clearly indicate that cross-linking is taking place in poly(**1**) domains, which ultimately leads to the formation of very rigid networks. At the same time, poly(MA) domains remain intact during this process. Swelling experiments also confirmed the formation of cross-linked structures. The original block copolymer BDA-2 is soluble in toluene and other organic solvents. After thermal treatment at 245 °C even for a short period of time (3 h), the polymer becomes insoluble but can swell to a certain degree. After prolonged heating (32 h), polymer samples become completely insoluble in organic solvents and do not exhibit any swelling, suggesting a high degree of cross-linking.

The SAXS analysis confirmed the retention of formed microstructures upon cross-linking (Figure 6). The primary scattering peak and higher order reflections ($\surd 3q_0$ and $\surd 7q_0$) were clearly distinguishable even for polymer samples annealed at 245 °C for 32 h, which had lost 50% of ethylene (TGA) and was fully cross-linked (DSC and swelling studies). While the domain size decreased slightly from 44 to 40 nm, the symmetry of the cross-linked microstructures remained the same. For block copolymers that underwent 50% retro-Diels–Alder reaction (which was enough to obtain a highly cross-linked network), the overall weight loss of less than 10% is expected due to the release of ethylene. Such a small change in volume of one of the domains did neither trigger a morphology transformation nor diminish a mechanical integrity of the sample.

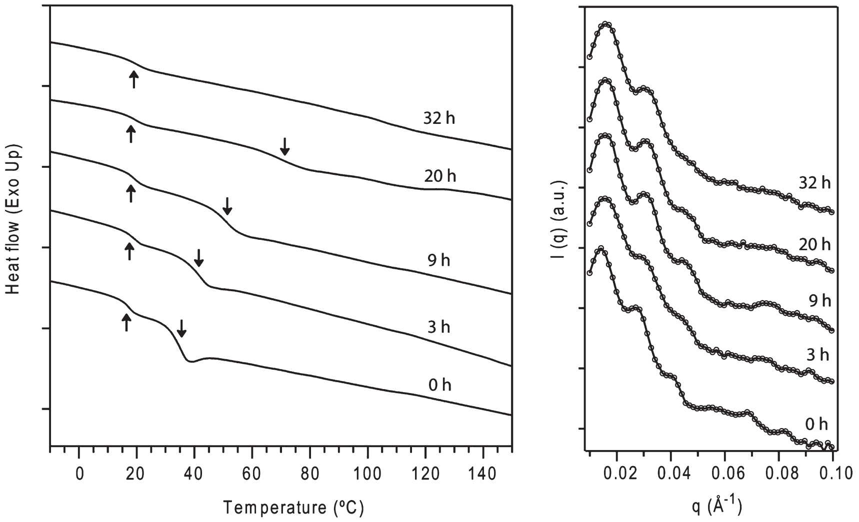


Figure 6. DSC (left) and SAXS (right) characterization of BDA-2 block copolymer after annealing at 245 °C. Up and down arrows indicate glass transitions of poly(MA) and poly(**1**) domains, respectively.

Cross-linking at 245 °C appears to be slow for practical use, but it is convenient for conducting detailed investigations of the chemical and physical transformation of the polymer samples during annealing, as shown above. It also allows for the control of cross-linking density to the highest degree. At higher temperatures, the rate of cross-linking was substantially higher. Thus, at 280 °C, poly(**1**) fully cross-linked in less than 1 h.

Conclusions

We have demonstrated a new cross-linking strategy via thermally triggered retro-Diels–Alder reaction of bicyclic diene polymers. A series of monomers with a norbornene skeleton and an exodiene structure were polymerized by traditional free-radical and living free-radical methods. Successful controlled polymerization of bicyclic dienes was mediated by TMPEPA nitroxide at 110 °C. Polymers with narrow molecular weight distributions were obtained from all studied monomers. Block copolymers poly(MA-*b*-**1**) were obtained by sequential nitroxide-mediated polymerization of methyl acrylate and **1**.

Free-radical polymerization of **1** proceeded predominantly by 1,4-addition at a rate that was 2.3 times faster than that of isoprene, despite the fact that monomer **1** had larger steric crowding around olefinic groups than isoprene. During copolymerizations of isoprene and **1**, both propagating radicals added much faster to monomer **1** than to isoprene, as determined by the calculated reactivity ratios. We attributed such high reactivity of **1** to the rigid *s-cis* coplanar conformation of the diene group.

Polymers of **1** and **3** underwent retro-Diels–Alder reaction upon heating with a concurrent release of ethylene. Thermally treated poly(**3**) transformed into a soluble, furan-containing polymer, while poly(**1**) cross-linked upon annealing at 245 °C. Retro-Diels–Alder reaction proceeded at much lower temperatures for poly(**3**) than poly(**1**) and did not take place at all for poly(**2**), all consistent with polymer repeat unit structures. Block copolymers of methyl acrylate and poly(**1**) microphase-separated into cylindrical and lamellae morphologies upon annealing at 180 °C, as confirmed by the SAXS analysis. Further thermal treatment of block copolymer samples at 245 °C under vacuum led to cross-linking of poly(**1**) domains and produced rigid, insoluble nanostructures. The morphologies and mechanical integrity of the samples was preserved during such a thermal treatment.

A new thermal cross-linking method presented here utilizes easily accessible bicyclic diene monomers. Living polymerization allows for the incorporation of thermally sensitive blocks in more complex polymer architectures, precursors for nanostructured materials. Retro-Diels–Alder reaction and subsequent cross-linking are very sensitive to the specific chemistry of the repeat units and thus bear great potential for designing polymers with specific cross-linking temperatures. This new methodology will be of great utility for the preparation of robust polymer-based nanostructures and other advanced materials.

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Supporting Information Available: Figures S1–S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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