

Ring-Opening Metathesis Copolymerization of Cyclooctene and a Carborane-Containing Oxanorbornene

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ABSTRACT: The incorporation of a silyl-protected oxanorbornene imide carborane (SONIC) in polyethylene-like materials is reported. These copolymers were obtained via ring-opening metathesis copolymerization of (SONIC) and cyclooctene followed by hydrogenation with *p*-toluenesulfonylhydrazide. The composition of the copolymer was varied by altering the feed ratio. Structural and thermal properties were investigated and compared with that of a model polymer so as to gauge the

impact on the inclusion of the silyl-functionalized carborane. An initial observation of the modification of the chain sequence upon changing solvent polarity is also discussed. Finally, the potential utilization of these materials as radiation shielding materials is mentioned. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 2557–2563, 2010

KEYWORDS: carborane; polyethylene; ROMP; thermal properties

INTRODUCTION With the growing desire to emulate the unique properties of natural organized systems (seashells,¹ teeth,² bones,³ etc.), the interest in hybrid organic-inorganic materials has soared. The development of processes, such as sol-gel chemistry or organic-templated assembly, is necessary to understand the underlying principles behind the properties of hybrid materials. Organic systems embedding chemically defined inorganic clusters seem to be a particularly promising class of materials.⁴ Studies in our group as well as several others have illustrated the advantages (chemical resistance, enhanced thermomechanical properties, directed assemblies, etc.) of hybrids that incorporate well-defined clusters of metal oxides or silicon oxides.^{5–8}

One class of inorganic clusters that are particularly interesting are the borane and carborane families. Based on studies by Stock in the early 1900's,⁹ the possibility to form inorganic clusters through self-catenation of boron has paved the way to numerous areas of research including the development of novel theories for chemical bonding. Although these clusters have, from their very start, interested material scientists for their great stability,^{10–13} there has been renewed interest in their incorporation in novel polymeric architectures. For example, Sneddon et al. have shown the possibility to use the inherent stoichiometry of a norbornene modified with decaborane side chain to obtain, via ring-opening metathesis polymerization (ROMP), polymeric precursors for the design of boron carbide nanowires by subsequent pyrolysis.^{14–18} Capitalizing on this chemistry, Malenfant et al. have demonstrated the possibility to synthesize diblock copolymers to obtain free-standing nanoscopic ceramics from pyrolysis of microphase-separated polymeric thin-films.¹⁹

These last two efforts are representative of the surge of interest for the ROMP of functionalized monomers because of the facile implementation brought about by catalysts developed by Grubbs et al.^{20–26}

The synthesis of a novel carborane-containing monomer **1** (silyl-protected oxanorbornene imide carborane: SONIC) and its subsequent incorporation in homopolymers and amphiphilic diblock copolymers by ROMP have been described previously.²⁷ Here, we report the incorporation of **1** in polyethylene-like materials by copolymerization with cyclooctene **2** (COE) followed by hydrogenation in the presence of *p*-toluenesulfonylhydrazide. The possibility to control the composition of the copolymer based on the feed ratio is demonstrated and the optimization of the hydrogenation conditions are also discussed. Thermal properties of the copolymers, and the evaluation of the influence of molecular weight, hydrogenation and composition upon these properties is also reported. For comparison purposes, a model compound was synthesized and homopolymerized to determine the influence of the silyl-functionalized carborane clusters on the physical properties of the polymer. Additionally, these polymers have elemental compositions making them suitable candidates for utilization in radiation shielding materials.

EXPERIMENTAL

Materials

All organic reactants and reagents were purchased from Aldrich Chemical and used as received unless specified otherwise. Toluene was dried over sodium with benzophenone

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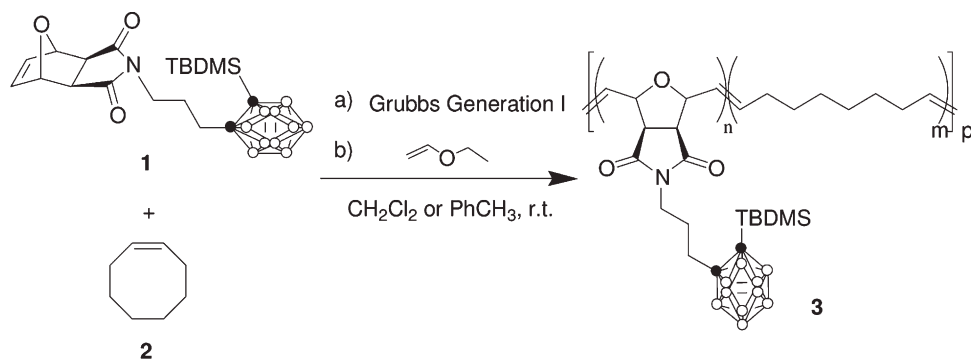


FIGURE 1 Ring-Opening Metathesis copolymerization of 1 and 2.

as an indicator. Dichloromethane was obtained through Fisher, distilled over calcium hydride and degassed with freeze-pump-thaw cycles. *O*-carborane was supplied by KatChem. Grubbs first generation (**GI**) was purchased from Strem Chemicals. Grubbs third generation (**GIII**) catalyst was synthesized according to the literature and stored under nitrogen atmosphere.²⁸ Monomer **1** was synthesized as previously described in the literature, the polymerization of this monomer by ROMP has also been described.²⁷ *o*-Xylene was passed through an activated alumina column prior to use, *p*-toluenesulfonylhydrazide was recrystallized from benzene.

The nomenclature for the different samples is as follows. Copolymers of **1** and **2** were named **3(XX)-T** or **3(XX)-D**, where T and D indicate the reaction solvents toluene or dichloromethane, respectively, and XX represents the molar percentage of monomer **1** in the feed. For example, a polymer with a targeted composition of 75 mol % of **1**, synthesized in toluene, is designated as **3(75)-T**. Subsequent hydrogenation of the materials will be indicated by an H in front of the descriptor. Therefore, the result of the hydrogenation of a polymer with 50 mol % SONIC originally synthesized in dichloromethane will be noted: **H-3(50)-D**.

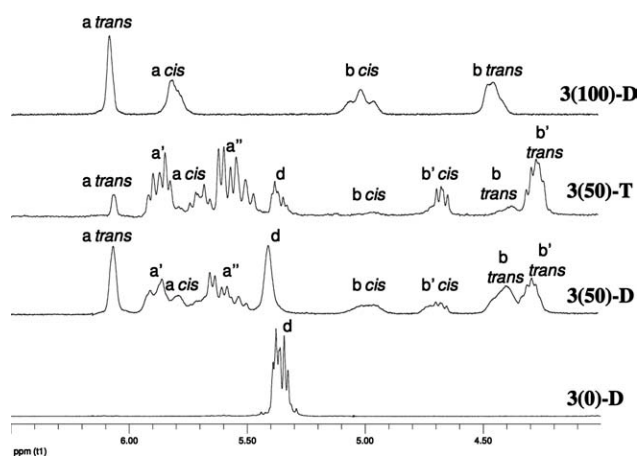


FIGURE 2 Illustration of the differences in alternation depending on solvent polarity. a: olefinic signal of polySONIC segments. b: allylic signal of polySONIC segments. d: olefinic signal of polyCOE segments.

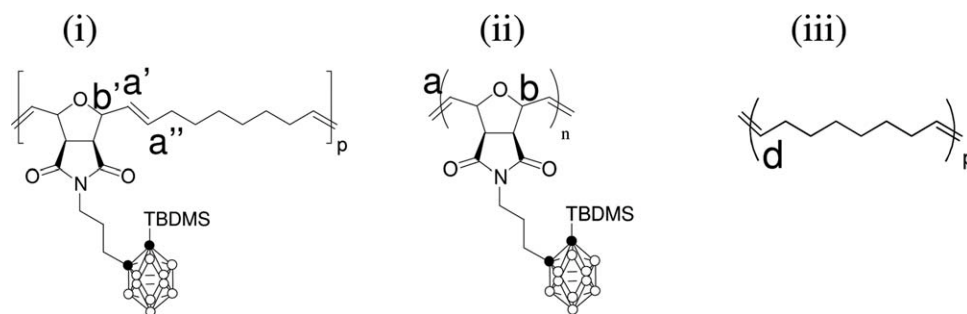
Instrumentation

Gel permeation chromatography (GPC) measurements for the polymers were performed in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min using a Knauer K-501 Pump with a K-2301 refractive index detector and a K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns at 40 °C. All other measurements were performed using a similar system with a column banks consisting of three Polymer Labs PLGel Mixed D columns at 40 °C. Molecular weights are reported relative to polystyrene standards. The ¹H NMR and ¹³C NMR were recorded at 300 and 100 MHz, respectively, on a Bruker NMR spectrometer at room temperature in deuterated chloroform. For ¹H NMR, the protons attached directly to the boron atoms of the carborane cage integrate for 10 protons as broad multiplets because of couplings with boron nuclei [δ (ppm) = 3.20–1.01 (br, 10H, BH)]. Thermogravimetric analyses (TGA) were performed on a TA-Instruments 2950 with a heating rate of 10 °C per min, sweeping temperatures ranging from 25 to 700 °C under inert atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC 822e and a DuPont Instrument 2910 with a heating rate of 10 °C per min from 25 to 250 °C for the homopolymers (**3(100)-D**, **H-3(100)-D**, **5** and **H-5**), and from –50 °C for the copolymers (**3(XX)** and **H-3(XX)**, with XX < 100).

Synthesis of 3(XX) with XX < 100

The polymerization of copolymers with different feed ratios was performed in either toluene or dichloromethane as follows. In a round bottom flask purged with nitrogen and equipped with a stir bar, the desired amount of **1** (463.70 g/mol) was dissolved in the reaction solvent so as to obtain a 0.2 mol/L solution. Using a syringe, the desired amount of COE was added. A solution of **GI** was then introduced such that the final molar concentration of catalyst would be 1000 times less than that of the combined monomers. The reaction was allowed to proceed for 24 h and was stopped by the addition of an excess of ethyl vinyl ether. The polymer was then precipitated in cold methanol and filtered over sintered glass. The stringy solid was then dried in a vacuum oven for 12 h at 40 °C. For NMR characterization see the discussion section.

SCHEME 1 (i) The hypothetical perfectly alternating structure of polymer 3(50), (ii) structure of the SONIC homopolymer, and (iii) polycyclooctene and their key observable proton shifts a, a', a'', b, and d.



Hydrogenation of the Polymers

The following is a typical experimental procedure performed. In a 50 mL round-bottom flask mounted with a condenser, the polymer (110 mg) and TSH (330 mg) were dissolved in 25 mL of *o*-xylene and the mixture was brought to reflux (130 °C) under constant agitation and with a slight nitrogen purge. After 2 h, the reaction was allowed to cool to 50 °C and was then precipitated in methanol. The NMR analysis for **H-3(100)-D**: ¹H NMR (CDCl₃): δ (ppm) = 3.79 (br s, 2H), 3.41 (br s, 2H), 3.11 (br s, 2H), 1.07 (s, 9H), 1.33 (s, 6H); ¹³C NMR (CDCl₃): δ (ppm) = 175.88, 81.15, 80.16, 76.20, 52.22, 37.80, 35.16, 31.10, 28.45, 27.55, 20.40, -2.47.

Synthesis of Exo-*N*-propyl-7-oxabicyclo[2,2,1]hept-5-ene-2,3-dicarboximide (**4**)

In a dry 500 mL flask, *exo*-7-oxonorborene imide (7.6 g, 46 mmol, 1 equiv.), propan-1-ol (3.8 mL, 51 mmol, 1.1 equiv.), and triphenylphosphine (13.3 g, 51 mmol, 1.1 equiv.) were dissolved upon stirring in 300 mL of freshly distilled dry THF. The flask was kept under nitrogen pressure and cooled down to 0 °C with an ice bath. After 5 min, diisopropylazodicarboxylate (DIAD) (3.2 mL, 16.26 mmol, 1.1 equiv.) was added and the solution turned yellow. The reaction was allowed to react overnight (16 h) affording a deep-yellow solution. The crude mixture was then concentrated *in vacuo* to obtain a sticky yellow paste. The paste was then redissolved in a minimum amount of THF and precipitated by dropwise addition into hexanes (800 mL). The precipitate was a white

TABLE 1 Conditions and Results for the Polymerization of Monomers **1** and **2**

Entry	M_n (g/mol) ^a	PDI ^a	Molar Ratios ^b		Catalyst
			SONIC	COE	
3(100)-D	58,600	1.09	100	0	GIII
3(75)-D	544,500	1.63	74	26	GI
3(50)-D	135,900	4.32	49	51	GI
3(25)-D	42,900	2.4	25	75	GI
3(75)-T	55,300	1.15	77	23	GI
3(50)-T	24,800	2	51	49	GI
3(25)-T	25,800	2.61	23	77	GI

^a As measured by GPC versus polystyrene standards.

^b As measured by ¹H NMR spectroscopy by comparing the integrations of the olefinic region with the silylmethyl peak at δ = 0.33 ppm.

powder with a slight reddish tint. The powder was then redissolved and precipitated a second time. The precipitate was then recrystallized from boiling methanol followed by cooling at -4 °C, affording 9.5 g of white powder (78% yield). ¹H NMR (CDCl₃): δ (ppm) = 6.51 (s, 2H, CH=CH), 5.27 (s, 2H, CHO), 3.45 (t, 2H, *J* = 7.2 MHz, NCH₂), 2.83 (s, 2H, CH=C=O), 1.60 (qt, 2H, *J* = 7.5 MHz, *J* = 7.2 MHz, CH₂CH₂CH₃), 0.88 (t, 3H, *J* = 7.5 MHz, CH₃); ¹³C NMR (CDCl₃): δ (ppm) = 176.37, 136.54, 80.91, 47.37, 40.53, 20.96, 11.15.

Polymerization of the Model Monomer **4** to Afford Polymer **5**

The polymerization of **4** was performed following the procedure used for the synthesis of **3(100)-D**. ¹H NMR (CDCl₃): δ (ppm) = 6.23 (br s, 0.95 H, CH-CH trans), 5.58 (br s, 1.05 H, CH=CH cis), 5.02 (br m, 1.05 H, CHO cis), 4.46 (br m, 0.95 H, CHO trans), 3.43 (br s, 2H, NCH₂), 3.35 (s, 2H, CH[sbond C[dbond O]), 1.72 (br s, 2H, CH₂CH₂CH₃), 0.89 (br s, 3H, CH₃); ¹³C NMR (CDCl₃): δ (ppm) = 175.72, 131.91, 81.10, 52.38, 40.52, 31.01, 11.27; GPC (PS std): M_n = 91,600 g/mol, PDI = 1.07.

Hydrogenation of the Model Polymer-H-5

The hydrogenation procedure was the same as that utilized to obtain **3**. ¹H NMR (CDCl₃): δ (ppm) = 3.82 (br s, 2H, CHO), 3.42 (br s, 2H, CH₂N), 3.11 (br s, 2H, CHC[dbond O]), 1.96 (br s, 4H, CH₂ backbone), 1.57 (br s, 2H, CH₂CH₂CH₃), 0.88 (br s, 3H, CH₃), GPC (PS std): M_n = 88,500 g/mol, PDI = 1.13.

RESULTS AND DISCUSSION

Copolymerization

ROMP has become over the years a very important tool for polymer chemists that wish to synthesize very precise

TABLE 2 Hydrogenation Results for the Polymers **3** Synthesized in Dichloromethane

Entry	M_n (g/mol) ^a	PDI ^a	Yield (%)
H-3(100)-D	43,900	1.05	88
H-3(75)-D	416,300	1.65	99
H-3(50)-D	115,000	3.92	98
H-3(25)-D	37,600	3.6	95

^a Measured by GPC against polystyrene standards.

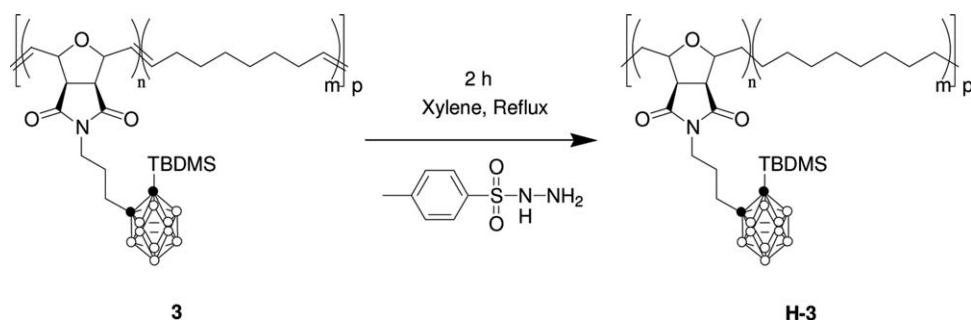


FIGURE 3 Conditions for the hydrogenation of polymer **3**.

macromolecular architectures.^{21,29–34} For example, our group has reported the homopolymerization of **1**, the present discussion will focus on the statistical copolymerization of monomers **1** and **2** (Fig. 1).²⁷ Previous work in our laboratory has pointed out the possibility to obtain strictly alternating structures by copolymerization of COE with oxanorbornene monomers.³⁵ Other laboratories have reported similar observations.³⁶ In the present investigation, it would be expected that consumption of the *exo* monomer **1**, would occur much more rapidly than that of monomer **2** leading to the formation of a tapered block copolymer. When the polymerization is carried out in dichloromethane, the presence of the two strong signals at $\delta = 6.1$ (a *trans*) and 5.3 ppm (d) characteristic of homopolymer sequences points towards this type of architecture (Fig. 2), although sequences with COE-rich and COE-poor segments cannot be entirely excluded. It is observed, however, for the copolymerizations of **1** and **2** conducted in toluene that the results point towards much more randomized structures where alternation, although not strict (Scheme 1), seems to prevail (Fig. 2). Another method to evaluate the extent of alternation consists in comparing the ratios of signals b *cis/trans* and b' *cis/trans* (Fig. 2). As can be observed for **3(50)-T**, and unlike **3(50)-D**, the signal of b' is much greater than the b counterpart, which further illustrates the tendency towards alternation obtained in the case of toluene as a solvent.

This notable difference can be in part accounted for by the difference in polymerization rate upon changing the solvent.

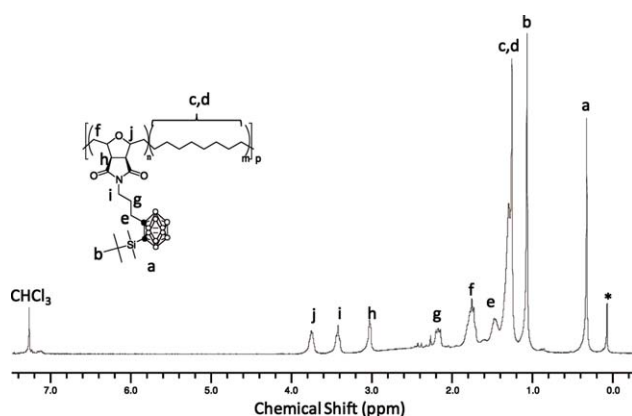


FIGURE 4 Proton NMR spectrum of **H-3(25)-D**.

An initiation rate increase of 30% has been observed in the literature upon altering the dielectric constant of the reaction medium when switching from toluene ($\epsilon = 2.38$) to dichloromethane ($\epsilon = 8.9$).³⁷ This phenomenon can be attributed to the stabilization of the product of the dissociation of the phosphine ligand from the ruthenium catalyst. This displacement of the equilibrium towards the dissociated species in conjunction with the intricate balance of ring-strain, sterics and electronics of the two monomers contributes to the tapering observed in dichloromethane. Conversely, in the presence of a less polar solvent, such as toluene, the metal alkylidene is much more tightly bound to the phosphine and remains in the active form for shorter times. This trend combined with the geometry and the electronic environment at the reaction site favors the alternation of monomers **1** and **2**.

As far as incorporation ratios are concerned, it can be observed that they are consistent with the feed ratios (Table 1). In the case of the copolymerizations in toluene, at ratios of SONIC:COE of 1:3 and 3:1 (Table 1, entries **3(75)-T** and **3(25)-T**), there are virtually no homopolymer sequences of the limiting monomer as indicated by the absence of characteristic resonance in the NMR spectra. In the case of dichloromethane as a reaction solvent, similar observations were made. The polymerizations in toluene seem to lead to the formation of much shorter chains. Again, this could be explained by the fact that the polymerization rate is accelerated in dichloromethane. Additionally, unlike ruthenium alkylidene bearing a N-heterocyclic carbene (NHC), complexes with two phosphines are much more prone to phosphine recoordination as they do not benefit from the donor effect of the NHC. If recoordination is disfavored by using a more polar solvent, it is expected that the molecular weights attained should be greater (Table 1). Also, since the catalyst spends much less time in a dormant state, the polymerization is less well-controlled leading to globally higher dispersity.

Hydrogenation

Previous studies in our group have demonstrated the possibility of using arylsulfonyl hydrazide at high temperatures to hydrogenate polyhedraloligomeric silsesquioxane-containing polymers.⁵ Several hydrogenation conditions were attempted on different polymers, changing solvent (toluene vs. xylenes), duration (from 1 to 16 h) and using the additive tri-*n*-

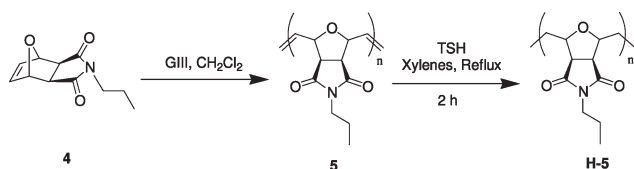


FIGURE 5 Synthesis of model polymers **5** and **H-5** to evaluate the influence of the silylcarborane cage on thermal properties.

propylamine. Although Hahn reported the necessity of using a high-boiling amine to prevent any side reaction,³⁸ in particular the protonation of olefinic sites upon formation of *p*-toluenesulfonic acid, it was observed that the amine actually contributed to a sharp decrease of molecular weight upon hydrogenation. This observation is believed to be a result of the degradation of the polymer. Although the mechanism is still unclear, it is suspected that the amine interacts with the silyl group which leads, in turn, to the alteration of the periphery of the carborane cluster.

Reaction temperatures and reaction times proved to have a key role on the outcome of the reaction. The results for the hydrogenation are reported in Table 2. The hydrogenation can be performed in reasonably high yield with virtually no remaining unsaturation as monitored by ¹H NMR spectroscopy (Figs. 3 and 4). Furthermore, no significant increase in dispersity was noted. Also, despite the net increase in molecular weight by addition of hydrogen onto the C=C double bonds, the apparent molecular weights of the hydrogenated materials by GPC are overall lower than their unsaturated counterparts. This phenomenon can be accounted for by the fact that the chain becomes more flexible as the double bonds are removed because of the free rotation about the newly formed carbon-carbon single bonds. This increase in the degree of freedom allows for the chain to adopt a much more compact conformation, and therefore, an apparently smaller hydrodynamic radius.

Thermogravimetric Analysis

The influence of molecular weight, unsaturations, and the composition (copolymer and presence of carborane) on the thermograms was investigated. Model polymers **5** and **H-5** were synthesized to evaluate the influence of the carborane cage on thermal properties (Fig. 5). To evaluate the influence

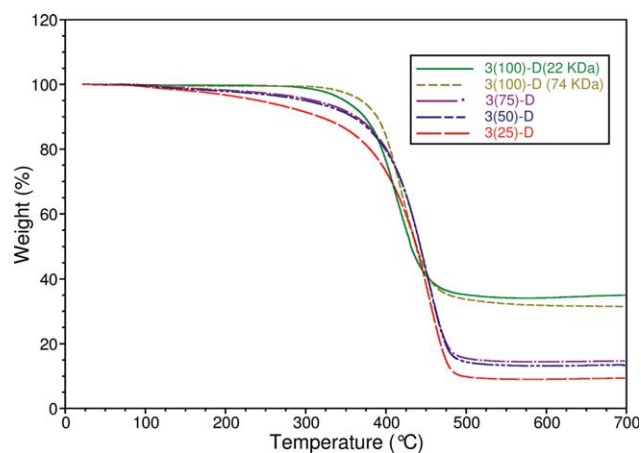


FIGURE 6 Superimposed gravimetric thermograms of the unsaturated polymers showing the independence of decomposition properties with molecular weight and the increase of both onset of decomposition and char yield with increase in carborane content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of unsaturation and molecular weight, two series of polymers were considered (**3** and **H-3**). Thermal decomposition for both series does not seem to be molecular weight dependent, as the thermograms are superimposable (Fig. 6). This superimposition stems from the fact that the polymers are above the critical molecular weight for which the chain length would play a role. As expected, the unsaturated polymer **3** shows a lower onset of decomposition temperature than **H-3**, as the presence of allylic protons undermines the thermal stability of the polymer (Table 3, Fig. 7). Nevertheless, the double bonds favor the formation of char through crosslinking, resulting in higher char yields. Also, not surprisingly, when comparing with the model compound **5**, the hydrogenated version, **H-5**, with the carborane cage leads to increased char formation upon pyrolysis for **3(100)-D**, resp. **H-3(100)-D** (Table 3). Additionally, and as expected, it can be noted that the char yield increases with the increase in carborane content and this is particularly noticeable when char formation is favored (i.e., when unsaturations are present). Also, the homopolymer of SONIC has a much higher onset of decomposition than the monomer (370 °C vs. 148 °C).

TABLE 3 Summary of the Thermogravimetric Analysis and Differential Scanning Calorimetry Results of **3**, **H-3**, **5**, and **H-5**

Entry	T_g (°C)	Onset of Decomposition (°C)	Char Yield	Entry	T_g (°C)	Onset of Decomposition (°C)	Char Yield
3(100)-D	153	370	31.6%	H-3(100)-D	145	423	15.5%
3(75)-D	99	310	14.6%	H-3(75)-D	88	410	11.0%
3(50)-D	78	300	13.2%	H-3(50)-D	^b	407	10.2%
3(25)-D	32	241	9.0%	H-3(25)-D	32	393	6.7%
3(0)-D	-60 ^a	^b	^b	H-3(0)-D	^b	^b	^b
5	131	396	9.8%	H-5	103	411	3.2%

^a According to ref. 22.

^b Not measured.

DSC Analysis

DSC analysis was used to study the effect of the new polymer structures and molecular weights on the observed thermal transition (glass transition temperature (T_g), melting temperature (T_m)). As observed for the TGA experiments, the molecular weights do not seem to affect the T_g (Fig. 8). However, a decrease by nearly 10 °C was observed for the hydrogenated version **H-3** with respect to their unsaturated counterparts **3**. This decrease can be explained by the free volume generated upon hydrogenation. The latter confers flexibility to the backbone as it allows for the rotation about the C—C single bond, thereby generating more free volume in the polymeric structure. This phenomenon is also observed in the case of the model compound.

CONCLUSIONS

We have reported the copolymerization of **1** and **2** to obtain polyethylene-like materials, which incorporate carborane pendant groups. The reaction conditions for the hydrogenation subsequent to the ROMP of the two monomers have been optimized. The possibility to control the composition of the copolymer has been highlighted as well as the influence of solvent polarity on the statistical polymerization. TGA has shown enhanced thermal properties upon increasing the fraction of monomer **1** in the feed. DSC analysis indicated the absence of crystallization of the boron clusters. Additionally, Wilson et al. have pointed out that polymeric materials are excellent candidates for space exploration because they combine light weight, adjustable thermomechanical properties and are relatively inexpensive to process.^{39,40} We believe that the synthetic approaches described here offer a level of control that could be tailored to match the protective requirements necessary for space travel.⁸ Simulation studies by Singleterry et al. have highlighted the potential of ¹⁰B

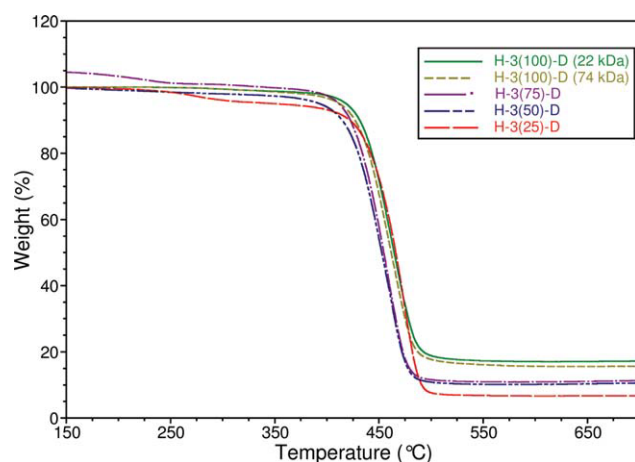


FIGURE 7 Superimposed gravimetric thermograms of the hydrogenated polymers showing the independence of decomposition properties with molecular weight and the increase of both onset of decomposition and char yield with increase in carborane content with less impact than their nonhydrogenated counterparts.

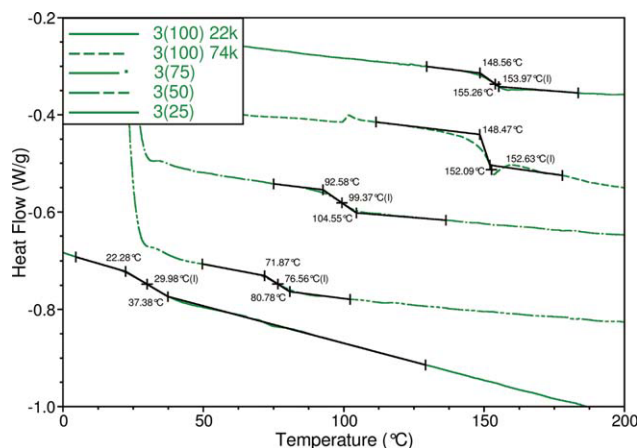


FIGURE 8 DSC thermograms of the series of polymers synthesized in dichloromethane.

loaded polyethylene as space-survivable materials, as they provide protection from fast neutrons and high mass ions.⁴¹ The elemental compositions used here allow for the thermalization of neutrons through inelastic collisions with the hydrogens along the polyethylene-like backbone as well as neutron capture because of the high capture cross section of ¹⁰B.^{41,42}

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