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Synthesis and characterization of B-C polymer hollow microspheres from a new organodecaborane preceramic polymer

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Abstract

A new poly (norbornenyldecaborane-co-hexadiene) (P(NB-co-DE)) copolymer as a kind of boron carbide preceramic polymer, was synthesized by the ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) reaction of 6-norbornenyldecaborane with 1,5-hexadiene. The synthesized polymer precursor which had good solubility and film-forming ability was freely soluble in most organic solvent and with a high ceramic yield of 74 % at 700 ºC. Furthermore, this polymer precursor was used to fabricate B-C hollow microspheres by microencapsulation. The prepared capsules with a diameter of about 570 μm had potential to obtain hollow B-C based ceramic microspheres, and they could be used in polymeric state or pyrolyzed ceramic forms.

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1. Introduction

Boron carbide is of great interest due to the low density, chemical inertness, high thermal stability, and excellent mechanical properties.[1-3] Recently, it can be used for high performance applications, including abrasive wear-resistant material, ceramic armor, neutron moderator, and potentially, for inertial confinement fusion (ICF) experiments.[4-5] Boron carbide materials can easily be prepared by classical carbothermal reduction or magnesiothermic reduction of boric oxides at high temperature,[6] but the formation of pure boron carbide in complex forms, such as films, fibers and microspheres, is difficult.[7] In 1976, Yajima et al. established the method to fabricate ceramics by preceramic polymers.[8] Then the technique of preceramic polymer conversion provided a way for preparing functional ceramic with complex forms,[9-10] because the solubility or fusibility of the precursor polymer allowed the shaping to be carried out at moderate temperatures and conventional polymer processing techniques.[10] Moreover, the composition of a suitable polymer could be controlled precisely with stoichiometry, which might be systematically varied to optimize ceramic properties.[11]

For boron carbide, decaborane ($B_{10}H_{14}$) with a high B proportion is the most widely used to produce kinds of polyborane compounds.[12] Sneddon and coworkers have shown new selective routes to boron carbide based on the use of the new polymer systems by using decaborane as the resource of boron atom.[13] They found that the $Cp_2ZrMe_2/B(C_6F_5)_3$ system polymerized efficiently to poly(6-hexenyl decaborane). Wei et al. reported the synthesis of poly(6-norbornenyldecaborane) and poly(6-cyclooctenyldecaborane) by employing ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) reaction.[14] Yu et al. also demonstrated that poly(6-hexenyldecaborane) and poly(6-norbornenyldecaborane could be obtained with decaborane in the mainchain by catalytic sequential hydroboration.[15]

However, these polymeric precursors are always with high rigidity which derives from the number of boron hydride cluster, so it is difficult to prepare boron carbide based films or microspheres with little defects. Accordingly, a straightforward synthesis adaptable to produce B-C polymer microspheres is of interest, the solubility and film-forming ability of the preceramic precursor are in a great demand.[16] The aim of this research was to design and synthesize a new kind of boron carbide preceramic polymer which combined the flexible groups in the polymer chain with 6-norbornenyldecaborane. Besides, the synthesized copolymer was used to prepare B-C polymer hollow microspheres by microencapsulation.

2. Experimental procedure

2.1 Materials

The Grubbs catalyst $Cl_2Ru(=CHPh)(PCy_3)(H_2IMes)$ (II) ((H_2IMes=1,3-dimesityl-4,5-dihydroimidazol-2-ylidene), Jingchun Reagent, Shanghai, China), decaborane (Kaimeike Chemical, Zhengzhou, China), 2,5-norbomadiene (Alfa Aesar, Shanghai, China), 1,5-hexadiene (J&K Scientific, Shenzhen, China), 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$, Chengjie Chemical, Shanghai, China) and ethyl vinyl ether (Jingchun Reagent, Shanghai, China) were used as raw materials. Dichloromethane (DCM, Kelong Chemical, Chengdu, China) was dried over by calcium hydride. Toluene (Kelong Chemical, Chengdu, China) and fluorobenzene (FB, Jingchun Reagent, Shanghai, China) were purified by distillation. N-hexane (Kelong Chemical, Chengdu, China), petroleum ether (Kelong Chemical, Chengdu, China) and polyvinyl alcohol (PVA, (M_w=13000-23000, 87-89% mole hydrolyzed), Sigma-Aldrich, Hannover, Germany) were all used as received without any further purification.

2.2 Synthesis of poly (norbornenyldecaborane-co-hexadiene)

In a procedure similar to that reported by Kusari et al.,[17] 10 mmol decaborane and 30 mmol 2,5-norbomadiene were reacted in a biphasic mixture of toluene (14 mL) and bmimBF_4 (3 mL) at 125 ºC for 24 h while being stirred vigorously enough to form an emulsion (Scheme 1). When the reaction was completed, the product was removed in the toluene layer. The 6-norbornenyldecaborane product was isolated through a silica gel column.

Then 6.25 mmol of 6-norbornenyldecaborane, 0.74 mL 1,5-hexadiene, 45 mL dichloromethane and 3 mol% Grubbs catalyst were sequentially added into a 100 mL two-necked round-bottomed flask. The polymerization reaction was carried out by stirring the mixed solution at 40 ºC for 6 h in the argon flow (Scheme 2). And the reaction was quenched by adding 1 mL ethyl vinyl ether. After that, the mixture was filtered through a short silica gel column, condensed, and precipitated by n-hexane. The resulted product was poly (norbornenyldecaborane-co-hexadiene) (P(NB-co-DE)).

2.3 Preparation of B-C hollow microspheres

Compound droplets (W1/O) were generated by a triple orifice droplet generator (shown in Fig. 1). Pure water was used as the inner phase, the synthesized copolymer P(NB-co-DE) dissolved in FB with the polymer mass fraction 30% was used as the middle phase in this work, and aqueous solution of 2 wt.% PVA was used as the outer phase. As shown in Fig. 1, the three fluids were delivered into the triple orifice droplet generator by three syringes, which were controlled by three pumps, respectively. Uniform double emulsion droplets could be generated at the end of the generator by the strong shearing force of external fluids and interfacial tension. And the generated compound droplets were collected in a cylindrical flask filled with PVA solution.

2.4 Characterization

^{1}H-NMR at 600 MHz was obtained by Avance 600 Fourier transform spectrometer (Bruker). All ^{1}H chemical shifts were measured relative to residual protons in the lock solvents and referenced to Me_4Si (0.00 ppm). Thermal decomposition of the copolymer up to 750 ºC in argon was performed by thermal gravimetric analysis (TGA, Pyris 1, Perkin Elmer). Molecular weight and its distribution were determined by gel permeation chromatography (GPC, Waters Model 150 chromatograph, Wyatt Technology Corporation). Both multiangle light scattering and differential refractive index (DRI) detector were employed with dimethylformamide (DMF) as a solvent. Glass-transition temperature (T_g) of the polymer was measured by a differential scanning calorimetry (DSC, Thermal Analysis Q2000, TA Instruments). The external morphology of the B-C hollow microspheres was observed by the optical microscope (VHX-600, Keyence). The morphologies and surface roughness were observed by scanning electronic microscopy (SEM, TM-1000, Hitachi).

3. Results and discussion

3.1 Properties of copolymer P(NB-co-DE)

Detailed molecular weight study was carried out in DMF with SEC-GPC. Fig. 2 presented the GPC results of the copolymer P(NB-co-DE). The weight-average molecular weight (M_w) was 5200 while the number-average molecular weight (M_n) was 3900, and the molecular weight distribution was about 1.318. In this figure, there was only one single peak with retention time and the molecular weight distribution was narrow, confirming that copolymerization reaction occurred in the reaction process. Furthermore, the precursor was well soluble in toluene, DMF, FB and tetrahydrofuran (THF), etc. The relatively low molecular weight was in favor of solubility and the narrow polydispersity index might be beneficial to the uniformity of preceramic polymer. Their good processabilities were particularly appealing aspects with regard to applications as precursor to boron carbide ceramic microspheres.

The molecular structures of monomer 6-norbornenyldecaborane and copolymer P(NB-co-DE) were further confirmed by ^{1}H-NMR spectrum (Fig. 3). As shown in Fig. 3(a), the multiplets and typical signals were highly consistent with the published literature.[17-18] And the ^{1}H-NMR spectrum of P(NB-co-DE) (Fig. 3(b)) showed multiple broadened peaks, indicating the complex polymer structure of the prepared precursor.[18] The chemical shifts ranging from 4.9 to 5.8 ppm were consistent with the unsaturated organic backbones (=CH), while the two sets of bridging hydrogens on the decaborane cage (BHB) could be attributed to the chemical shifts at -1.68 and -2.08 ppm. According to integration date, the relative value of =CH/BHB was about 3:4, while the corresponding ratio of the homopolymer poly (6-norbornenyldecaborane)[18] was 2:4. The content of the =CH units of the synthesized polymer significantly increased, which also meant a copolymer product was successfully synthesized.

Fig. 4 showed the TG results of the copolymer P(NB-co-DE) from 50 to 750 ºC. It could be seen that the pyrolysis mechanism of the polymer consisted two main steps. An initial weight loss of about 12% was observed in the temperature range 100 to 200 ºC, which could be attributed to the loss of low molecular weight products. The second step between 250 ºC and 650 ºC referred to the degradation of the precursor. And the weight loss nearly completed at 700 ºC with the ceramic yield of 74%. This result demonstrated that P(NB-co-DE) displayed excellent thermal properties as well as the homopolymer of poly(6-norbornenyldecaborane) branched with decaborane.[14] The proper reason might be that the structure of ring backbone in the polymer chain played an important role in carbon retention. And the cross-linking reactions among the flexible chains including numbers of double bonds might be occured under a relatively high temperature, which would increase the char yield of the polymer.[19]

The DSC result of the copolymer P(NB-co-DE) was shown in Fig. 5. And it could be observed that the T_g of the polymer was about 43 ºC which was lower than its initial decomposition temperature. So this copolymer P(NB-co-DE) could be processed to any desired forms before thermal conversion to the final ceramic materials.[20] As for those, this copolymer had a great potential as precursor to fabricate functional boron carbide ceramics with complex forms. Comparing with the TG results, the exotherm in the range 100-150 ºC might be attributed to the release of the small molecule.

3.2 Properties of monodisperse B-C polymer hollow microspheres

The formation of the monodisperse double emulsion drops with P(NB-co-DE) was shown in Fig. 6. The outer diameter and thickness of the B-C shells were set as 770 μm and 260 μm, respectively, as determined from the optical images. The double emulsions generated were stable through the solidifying process. Fig. 7 presented the SEM morphologies of the prepared microspheres. In Fig. 7(a), it could be seen that the capsules appeared to change little with time and they maintained their monodispersity and sphericity. And the surface of the shells was highly porous with pore diameters in the range of 1-5 μm as shown in Fig. 7(b). The porosity in the shells made these capsules mechanically fragile, [21] which resulted in deformed shells during cutting off for the observation for the microstructures. The shell had a thickness of 65 μm and the diameter was about 570 um. It might be possible to use these capsules as containers by filling them with biomaterials or some other materials. [22] Besides, the surface roughness and porosity condition of the shells might be changed after radiation or heat treatment.

4. Summary

A new kind of polyborane copolymer P(NB-co-DE) with good solubility and film-forming ability has been synthesized by the ruthenium-catalyzed ROMP reaction. The ceramic yield and T_g of the copolymer were 74 % at 700 ºC and 43 ºC, respectively. Monodisperse B-C hollow microspheres were also fabricated with the synthesized copolymer P(NB-co-DE) via microencapsulation. The prepared capsules with a diameter of about 570 μm had porosity that was open to the exterior with pore diameters in the range of 1 to 5 μm. This work demonstrated that it was possible to use microfluidics to process preceramic polymers to generate monodisperse B-C polymer hollow microspheres, which was potential to obtain hollow B-C based ceramic microspheres. And application of these hollow microspheres for the preparation of boron carbide ceramic microspheres is ongoing in our group.

Acknowledgments

This work was supported by the foundation of China Academy of Engineering Physics (No. 2013B0302053).

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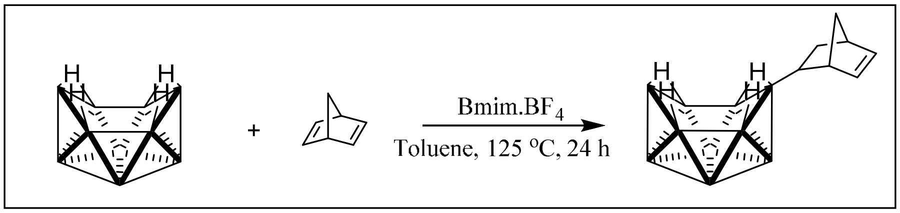
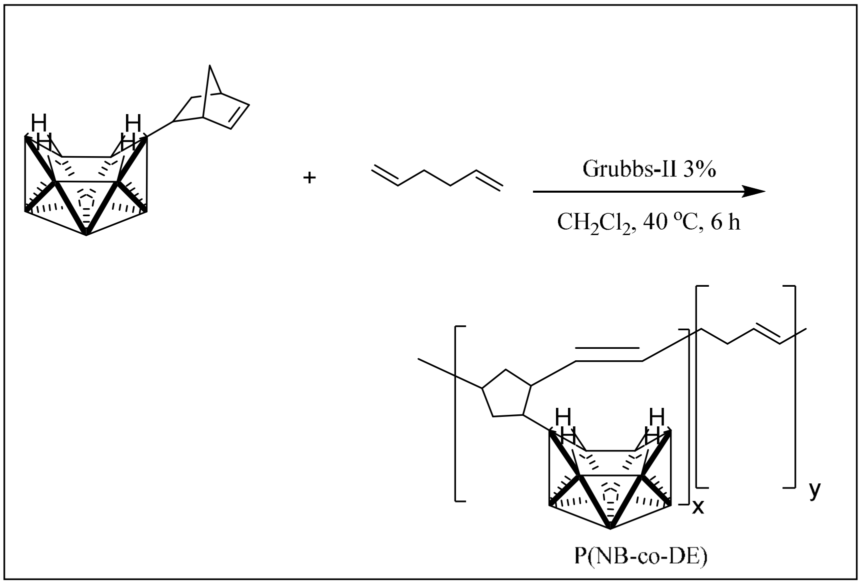


Scheme 1 Hydroboration for the synthesis of 6-norbornenyldecaborane



Scheme 2 Copolymerization of 6-norbornenyldecaborane and 1,5-hexadiene

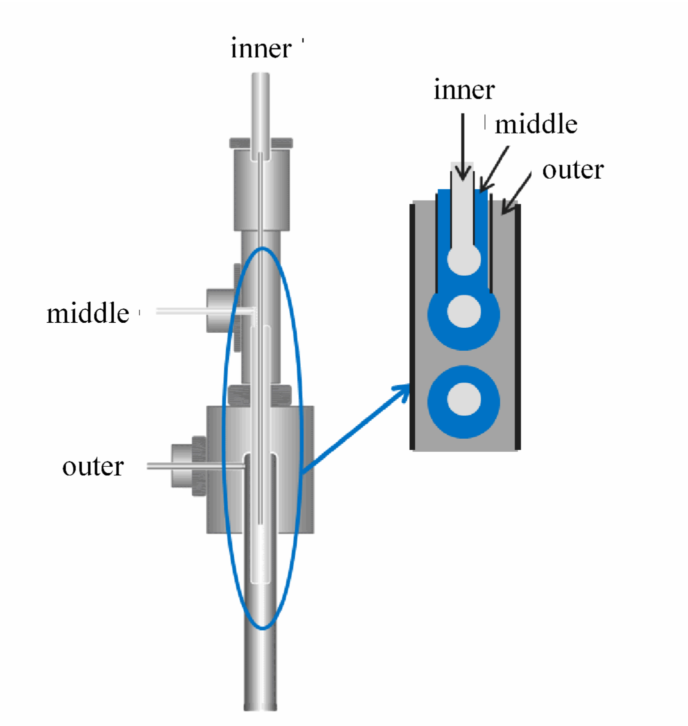


Fig. 1 The schematic illustration of generating double emulsion droplets by a triple orifice droplet generator

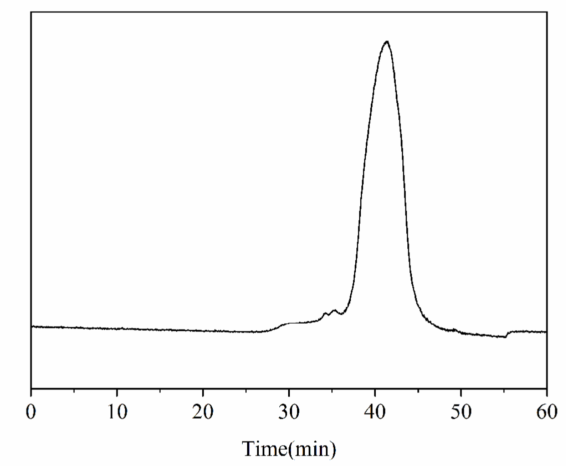


Fig. 2 GPC results of the copolymer P(NB-co-DE).

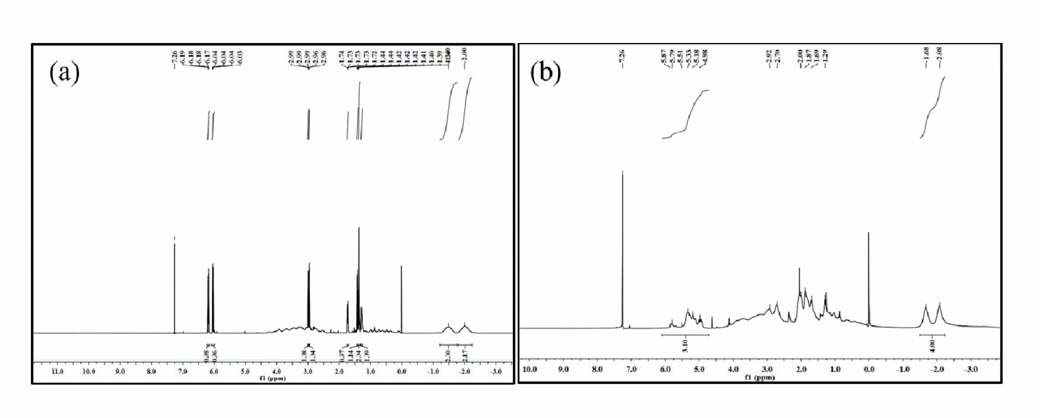


Fig.3 ^{1}H-NMR spectra of (a) monomer 6-norbornenyldecaborane and (b) copolymer P(NB-co-DE)

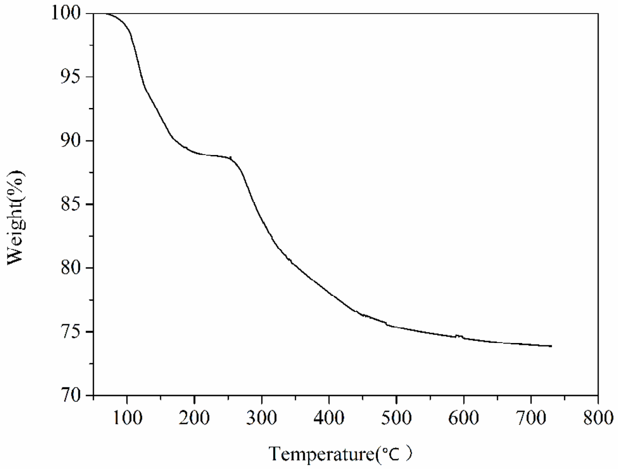


Fig. 4 TG results of the copolymer P(NB-co-DE).

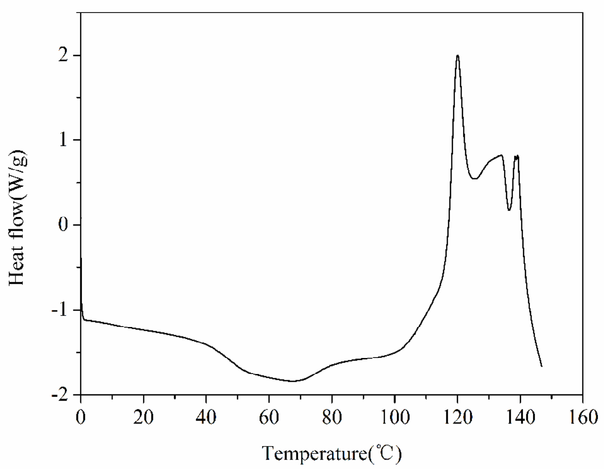


Fig. 5 DSC results of the copolymer P(NB-co-DE).

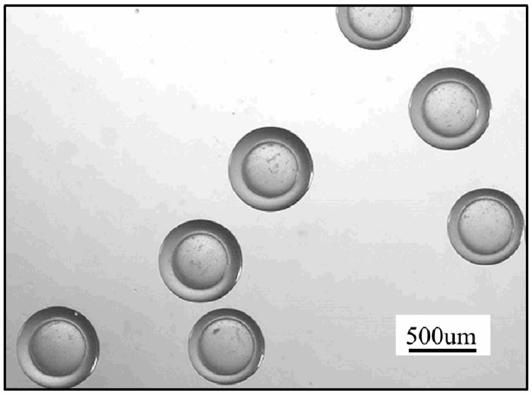


Fig. 6 Optical images of the B-C preceramic double emulsion drops.

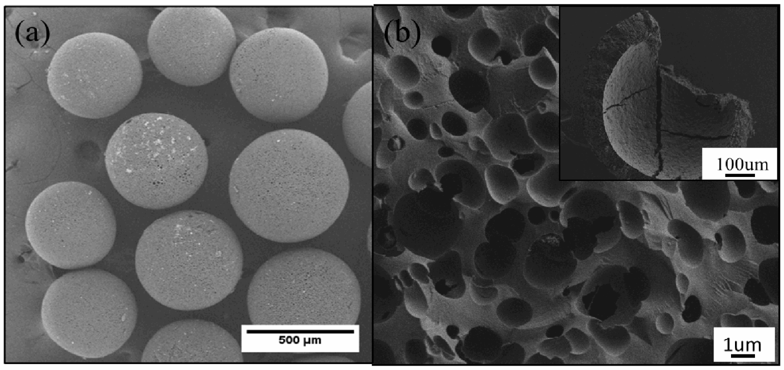


Fig. 7 SEM morphologies of the prepared microspheres.