

Synthesis and Characterization of Bornylene-sulfur Dioxide Polysulfone Resin

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Abstract: Bornylene-sulfur dioxide polysulfone resin (BE-SO₂) was synthesized by free radical copolymerization of monomers SO₂ and bornylene (BE) which synthesized from α -pinene. Similarly, BE-SO₂-Ma and BE-SO₂-St were synthesized using BE, SO₂, maleic anhydride (MA) as monomers and BE, SO₂, styrene (St) as monomers respectively. Effects of operating conditions such as monomer ratio, polymerization temperature and reaction time on the copolymer yields are discussed. The results showed that the optimum reaction conditions are as follows: reaction temperature -20 °C, reaction time 4 h, $n(\text{BE})$ 1 mmol, $n(\text{BE}) : n(\text{Ma})$ 1 : 1, $n(\text{BE}) : n(\text{St})$ 1 : 1, CYC as solvent and volume 4 mL, and the highest yield of BE-SO₂, BE-SO₂-Ma, BE-SO₂-St are 70 %, 64 % and 71 %, respectively. The structure of the copolymers were characterized by FT-IR, GPC, DSC, EA and SEM. BE-SO₂ was a black solid powder with weight average molecular weight (M_w) of 1 069, number average molecular weight (M_n) of 376, and T_g of 134.5 °C; BE-SO₂-Ma polysulfone resin is a dark brown solid powder with M_w of 1 576, M_n of 402 and T_g of 152.0 °C; BE-SO₂-St polysulfone resin is a tan solid powder with M_w of 33 054, M_n of 952 and T_g of 174.8 °C.

Key words: bornylene; sulfur dioxide; free radical polymerization; polysulfone resin

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冰片烯-二氧化硫聚砜树脂的合成及表征

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摘要: 以 α -蒎烯为原料合成冰片烯。以冰片烯(BE)、二氧化硫(SO₂)为单体, 采用自由基聚合方法合成了冰片烯-二氧化硫聚砜树脂(BE-SO₂), 用同样的方法分别以冰片烯(BE)、二氧化硫(SO₂)、马来酸酐为单体和以冰片烯(BE)、二氧化硫(SO₂)、苯乙烯(St)为单体, 合成冰片烯-二氧化硫-马来酸酐(BE-SO₂-Ma)以及冰片烯-二氧化硫-苯乙烯(BE-SO₂-St)两种三元共聚物。讨论了单体配比、聚合反应的温度和时间对共聚物得率的影响, 结果表明: $n(\text{BE})$ 1 mmol, $n(\text{BE}) : n(\text{Ma})$ 1 : 1, $n(\text{BE}) : n(\text{St})$ 1 : 1, 加入 4 mL CYC 作溶剂, 在 -20 °C 条件下反应 4 h, BE-SO₂, BE-SO₂-Ma, BE-SO₂-St 得率最高, 分别为 70 %、64 % 和 71 %。此外, 分别用 FT-IR、GPC、DSC、EA 和 SEM 等方法对共聚物结构进行了表征, BE-SO₂ 为粉末状黑色固体, 重均相对分子质量(M_w)为 1 069, 数均相对分子质量(M_n)为 376, T_g 为 134.5 °C; BE-SO₂-Ma 共聚物为粉末状黑褐色固体, M_w 为 1 576, M_n 为 402, T_g 为 152.0 °C; BE-SO₂-St 共聚物为粉末状黄褐色固体, M_w 为 33 054, M_n 为 952, T_g 为 174.8 °C。

关键词: 冰片烯; 二氧化硫; 自由基聚合; 聚砜树脂

The increasing shortage of non-renewable resources such as oil and mineral makes it more and more important for searching substitutes. Developing renewable sources is the best solution to relieve the problem of resources crisis in the whole world. Turpentine is a renewable natural resource distilled from pine gum. It is

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abundant in China with the output of over 1 000 kt per year^[1-6]. Turpentine was used as raw materials to synthesis a series of novel functional polymers such as polysulfone resin which is significant not only to science, but also to industry. This way will promote the comprehensive utilization of renewable resources and develop the deep processing of turpentine products, as well as provide a new approach of comprehensive use of SO₂ gas which pollutes the environment.

1 Experimental

1.1 Materials and facilities

GC analyses were carried out using an Agilent 6890N gas chromatograph equipped with FID detectors. T_g was determined with a DSC-60A using Al₂O₃ as standard sample. FT-IR spectra were measured with a Nicolet 380 infrared spectrometer. Molecular weight was measured with a Waters 515 GPC using PS ($M_w = 900 \sim 1.74 \times 10^6$ g/mol, $D < 1.1$) as standard sample and THF as solvent. Elemental analyses were determined with a Vario EL II elemental analyzer. Morphological changes of polymer were recorded with a Quanta 200 SEM.

All known compounds were identified by comparison of their physical and spectral data with those in the literatures. α -Pinene (97.29 % ,GC) was purchased from Guangdong Deqing Forestry Chemical Factory and rectified under vacuum. SO₂ were purchased from Chemistry Company; maleic anhydride (Ma) and styrene (St) were distilled from CaH₂, other reagents were of A. R. grade and used without further purification.

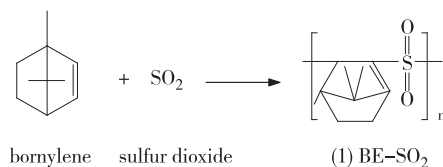
1.2 Preparation of bornylene (BE)

According to the literature methods^[7-9], BE was prepared from α -pinene .

Colorless, transparent crystal, yield 74.5 %, purity 95.3 % (GC); m. p. 111.0~114.0 °C, b. p. 146.0~147.0 °C; ¹H NMR (CDCl₃, 300 MHz): δ : 0.70~1.0 (s, 9H), 1.20 (m, 2H), 1.50~1.80 (t, 2H), 2.30 (s, 1H), 5.70 (d, 1H), 5.90 (t, 1H); IR (KBr, cm⁻¹): 3010 (=CH, $v_{asC=C}$), 2964 (—CH₃, v_{asC-H}), 2879 (—CH₃, v_{sC-H}), 1464 (—CH₂, δ_{sC-H}), 1389 (=CH, δ_{sC-H}), 717 (=CH, $\delta_{sC=C}$).

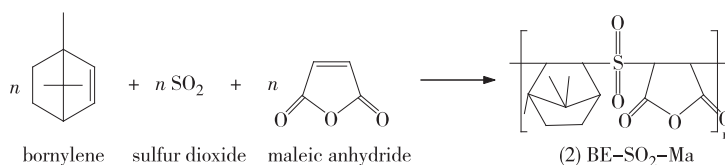
1.3 Copolymerization of BE and SO₂

Solution of BE (1 g, 1 mmol) in 4 mL cyclohexanone (CYC) was introduced into a 50 mL three-neck flask at -20 °C. The flask was purged three times with nitrogen, and then filled with SO₂, stirred for 5 h. The generated mixture was distilled under reduced pressure. A dark brown solid of 0.70 g BE-SO₂ polysulfone resin was obtained.

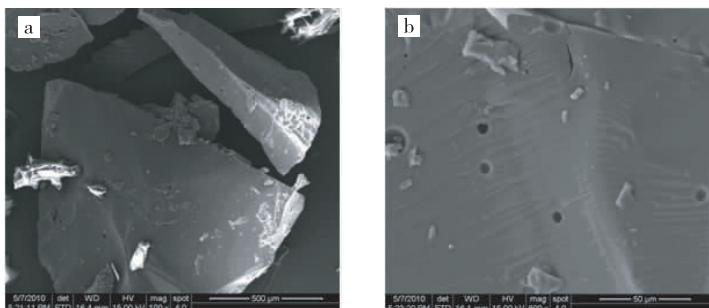


1.4 Copolymerization of BE, Ma and SO₂

Solution of BE (1 g, 1 mmol) and Ma (0.69 g, 1 mmol) in 4 mL CYC was introduced into a 50 mL three-neck flask at -20 °C. The flask was purged three times with nitrogen, and then filled with SO₂, stirred for 5 h. The generated mixture was distilled under reduced pressure. A brown solid of 0.64 g BE-SO₂-Ma polysulfone resin was obtained.



1320 – 1225 ($-\text{C}-\text{S}$, $v_{\text{C}-\text{S}}$); GPC(PS): $M_w = 1069$, $M_n = 376$; EA: Anal. calcd for $(\text{C}_{10}\text{H}_{16}\text{SO}_2)_n$: C 60, H 10.8, O 16.0, S 16.2; found C 66.7, H 9.1, O 10.8, S 13.8.

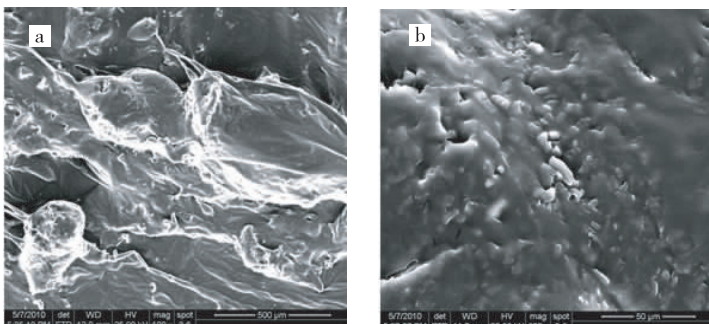


a. $\times 100$; b. $\times 10$

Fig. 1 SEM of BE-SO₂

2.4.2 BE-SO₂-Ma characterization BE-SO₂-Ma yield is 64 % and T_g is 152.0 °C.

SEM: Viscous liquid with numerous blocky-shaped particles (Fig. 2); IR (cm^{-1}): 2928 ($-\text{CH}_3$, $v_{\text{asC}-\text{H}}$), 2871 ($-\text{CH}_3$, $v_{\text{sC}-\text{H}}$), 1444 ($-\text{CH}_2$, $v_{\text{sC}-\text{H}}$), 1324 – 1224 ($v_{\text{C}-\text{S}}$), 1722 ($v_{\text{C}=\text{O}}$); GPC(PS): $M_w = 1576$, $M_n = 402$; EA: Anal. calcd for $(\text{C}_{14}\text{H}_{18}\text{SO}_5)_n$: C 68.9, H 7.9, O 5.7, S 8.7; found C 56.4, H 6.0, O 10.7, S 10.8.

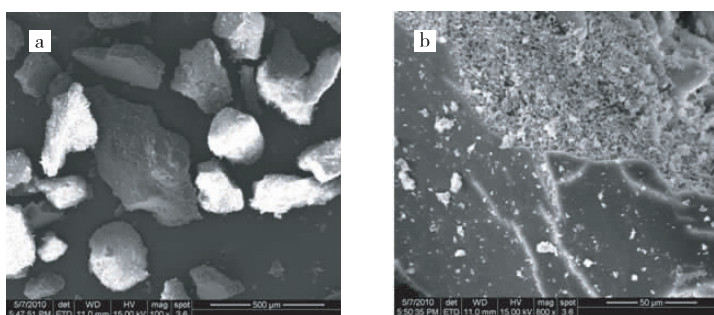


a. $\times 100$; b. $\times 10$

Fig. 2 SEM of BE-SO₂-Ma

2.4.3 BE-SO₂-St characterization BE-SO₂-St yield is 71 % and T_g is 174.8 °C.

SEM: Granular solid with loose surface (Fig. 3); IR (cm^{-1}): 3061, 3029 (aryl, $v_{\text{C}-\text{H}}$), 2926 ($-\text{CH}_3$, $v_{\text{asC}-\text{H}}$), 2853 ($-\text{CH}_3$, $v_{\text{sC}-\text{H}}$), 1454 ($-\text{CH}_2$, $\delta_{\text{sC}-\text{H}}$), 1320 – 1226 ($v_{\text{C}-\text{S}}$), 698 (single substituted benzenes, $\tau_{\text{C}-\text{H}}$). GPC(PS): $M_w = 33054$, $M_n = 925$; EA: Anal. calcd for $(\text{C}_{18}\text{H}_{24}\text{SO}_2)_n$: C 75.5, H 6.6, O 4.2, S 4.7; found C 71.1, H 7.9, O 10.5, S 10.6.



a. $\times 100$; b. $\times 10$

Fig. 3 SEM of BE-SO₂-St

3 Conclusions

A series of novel polysulfone resins were synthesized by free radical copolymerization. The effects of operating conditions were studied as well. The optimum reaction conditions are as follows: reaction temperature $-20\text{ }^{\circ}\text{C}$, reaction time 4 h, $n(\text{BE})$ 1 mmol, $n(\text{BE}) : n(\text{Ma})$ 1 : 1, $n(\text{BE}) : n(\text{St})$ 1 : 1, CYC volume 4 mL. The highest yields of BE-SO₂, BE-SO₂-Ma, BE-SO₂-St are 70%, 64% and 71%, respectively. All of them were characterized with GC, DSC, SEM, FT-IR, GPC and EA. BE-SO₂ polysulfone resin is a black solid powder with weight average molecular weight (M_w) of 1 069, number average molecular weight (M_n) of 376, BE-SO₂-Ma polysulfone resin is a dark brown solid powder with M_w of 1576, M_n of 402. BE-SO₂-St polysulfone resin is a tan solid powder with M_w of 33 054, M_n of 952. Finally, results indicated that the molecular weight of polymer was increased when adding another monomer such as Ma or St during the copolymerization of BE and SO₂.

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