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Well-Defined Renewable Polymers Derived from Gum Rosin

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Synthesis of new polymeric materials from renewable natural resources has become a rapidly growing area, as these materials could potentially replace or partially replace environmentally and energy unfavorable plastics derived from petroleum chemicals.[1−6] However, applications of renewable polymers are significantly behind petroleum-derived polymers, partially because of relative high cost and limitations in the monomer resources and therefore derived polymers. Thus, the development of novel low-cost and scalable monomers from renewable resources is essential.[7−12]

We have focused on developing a new class of renewable polymers using gum rosin due to its abundance, low cost, and its potential ability to be derivatized into polymerizable monomers. Produced more than 1 million tons annually, crude rosin and gum rosin, whose major components are resin acids (primarily abietic acid) with characteristic hydrophenanthrene rings, are exudates from pine trees and are generally used as ingredients for inks, vanishes, adhesives, cosmetics, medicines, chewing gums, etc.[13−15] However, the use of rosin as renewable resources has been mostly focused on step-growth polymerization to prepare low molecular weight polymeric materials.[16−21] Controlled radical polymerization (CRP) of monomers derived from gum rosin has not been studied, partially due to the absence of highly pure polymerizable vinyl monomers.[22−24] CRP allows to prepare well-defined polymers with controlled molecular weight, functionality, and architectures, which can enable one to develop more advanced materials such as thermoplastic elastomers and composites.[25−27] Herein we report the synthesis of high-quality rosin-derived vinyl monomers and the first preparation of well-defined rosin-derived polymers using atom transfer radical polymerization (ATRP).

We chose commercial dehydroabietic acid (DHAA, a racemic mixture) as our starting rosin materials since the aromatic ring in the hydrophenanthrene ring structure makes it more stable than abietic acid, while the functional carboxylic acid group allows the derivatization of various vinyl monomers.[22−24] However, most DHAA from commercial sources contain ∼5−10% unknown impurities (GS-MS data, Figures S1−S4), which turned out to be difficult to separate out. However, after derivatization of DHAA into vinyl monomers, we were able to remove all impurities readily through simple column chromatography. Under this scenario, four rosin-based acrylate and methacrylate monomers were synthesized (Scheme 1). Different spacers were placed between the vinyl group and dehydroabietic group in order to vary the steric effect imparted onto the vinyl group, which could have significant influence on the control of polymerization. Moreover, thermal properties (e.g., glass transition temperature (T_g)) of resulting polymers can be finely tuned. For dehydroabietic acrylate (DAA),[28] the dehydroabietic group is connected directly to the vinyl ester group, while dehydroabietic butyl acrylate (DABA) has the longest spacer in between.

DAA was prepared from acryloyl chloride and dehydroabietic alcohol, which was obtained by reduction of dehydroabietic acid with sodium borohydride. For other monomers (dehydroabietic ethyl acrylate (DAEA), DABA, dehydroabietic ethyl methacrylate (DAEMA)), dehydroabietic acid was first converted into acyl chloride under oxalyl chloride followed by in-situ esterification reaction with hydroxyl groups of corresponding (meth)acrylates. Impurities were removed by column chromatography. The structures of all monomers were confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectra (see Supporting Information). Figure 1 shows clear evidence of high purity of vinyl monomers, as confirmed from chemical shifts of vinyl, aromatic, methylene protons, and those protons next to the aromatic ring. All integrations of NMR spectra matched very well. From the two-dimensional correlation spectroscopy (COSY) study of ^{1}H NMR (Figures S5 and S6), the region between 1 and 2.5 ppm is also clearly assigned to the proton on the hydrophenanthrene ring. To the best of our knowledge, this is the first report on the synthesis of highly pure vinyl monomers derived from gum rosin.

Copper-catalyzed ATRP of all vinyl monomers was carried out in various conditions, and the results are summarized in Table 1. Gel permeation chromatography (GPC) traces of poly(dehydroabietic acrylate) (PDAA) were broad and multimodal with high polydispersity index (PDI = 3.65) (run 1 in Table 1, Figure S7), suggesting an uncontrolled polymerization, most likely due to dominating steric hindrance of side groups. The polymerizations of DAEA and DABA were first carried out in anisole with the use of copper(I) bromide and tris[2-(dimethylamino)ethyl]amine (Me_6Tren) as the catalyst and ligand. However, both polymerizations resulted in low molecular weight (< 7000 g/mol) after 48 h (not shown). The use of the more polar solvent tetrahydrofuran (THF) significantly increased the polymerization rate while maintaining PDI < 1.3. After 16 h, the molecular weight was 11 500 and 21 500 g/mol for poly(dehydroabietic ethyl acrylate) (PDAEA) and poly(dehydroabietic butyl acrylate) (PDABA), respectively (runs 2 and 3 in Table 1). The higher molecular weight of PDABA was consistent with less hindrance due to longer spacer between rosin moiety and vinyl group. The representative GPC traces are shown in Figure 2. The acrylate rosin polymers had a monomodal symmetric elution curve, indicating well-controlled polymerization. The rate enhancement in more polar solvents could be due to improved solubility of catalysts, which has been observed in different systems.[25,29,30]

We then carried out ATRP of methacrylate monomers (DAEMA) derived from rosin. Under the use of the same solvent (THF) as used for acrylate monomers, the polymerization of DAEMA was much faster than that of acrylate. 80% conversion was achieved within 24 h with a molecular weight of 32 900 g/mol for poly(dehydroabietic ethyl methacrylate) (PDAEMA) (run 4 in Table 1). However, the polymerization was not controlled as the PDI was as high as 1.6. Then we performed the polymerization with the use of less polar solvent: anisole. The reaction was slower but with much better control (run 5 in Table 1). The PDI was about 1.33. The GPC trace showed a symmetric single peak throughout the polymerization (Figure 2). Although the role of the solvent in the polymerization system is currently under

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investigation, some solvent-assisted side reactions such as elimination of HBr from poly(methacrylic halide)s could occur in more polar solvents.[25,29,30] It is worth noting that most of the molecular weight determined by GPC was much lower than that obtained by ^{1}H NMR analysis, suggesting that rosin-derived polymers may have significantly different hydrodynamic volume compared to polystyrene calibration standards, probably due to large dehydroabietic side groups.

^{1}H NMR spectra (Figure 3) of acrylate and methacrylate polymers show that the characteristic signals of vinyl protons from monomers at 5.4−6.5 ppm disappeared, accompanied by the appearance of broad peaks at 1−2.5 ppm corresponding to $-CH_2-CH-$ protons from the polymer backbone. All other peaks of dehydroabietic side groups were broader with nearly same chemical shifts as those of the monomers.

The thermal properties of PDAEA, PDABA, and PDAEMA polymers were characterized with the aid of differential scanning calorimetry (DSC) (Figure 4). All polymers exhibited typical thermoplastic behaviors, with no melting observed. The glass transition temperatures (T_g) showed a dependence of chemical structures of backbone and side groups. The methacrylate polymer (PDAEMA) showed highest $T_g \sim 90$ °C, while lowest T_g (~22 °C) was observed from acrylate polymers with longest spacers between side groups and backbone (PDABA), about 20 °C lower than that of PDAEA. This was in agreement with the concept that the longer spacer reduced the rotation barriers of acrylate polymers and decreased the T_g. Thermogravimetric analysis (TGA) of these different polymers was carried out under N_2 (Figure S8). All polymers showed two-stage weight loss behavior.

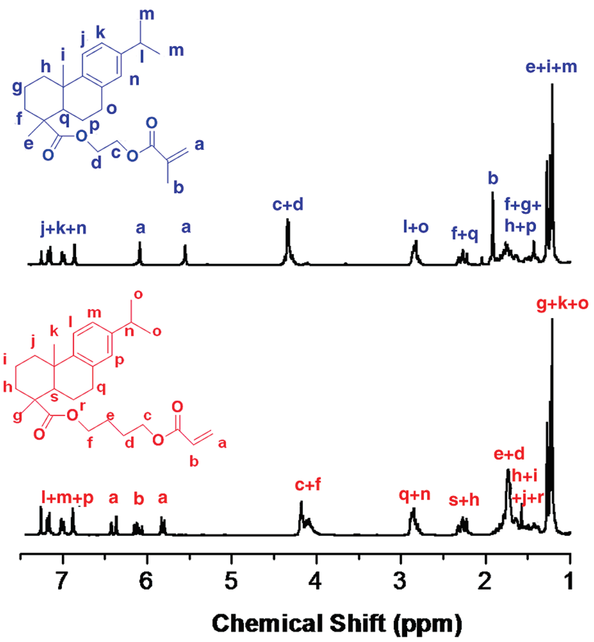

Figure 1. ^{1}H NMR spectra of vinyl monomers derived from rosin.

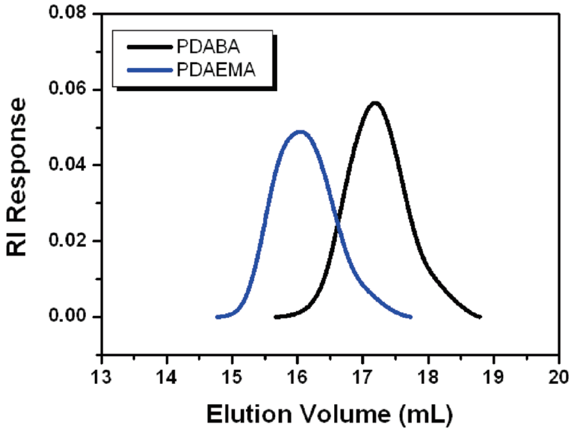

Figure 2. GPC traces of PDABA and PDAEMA prepared by ATRP (corresponding to runs 3 and 5 from Table 1, respectively).

Scheme 1. Synthesis of Vinyl Monomers from Gum Rosin

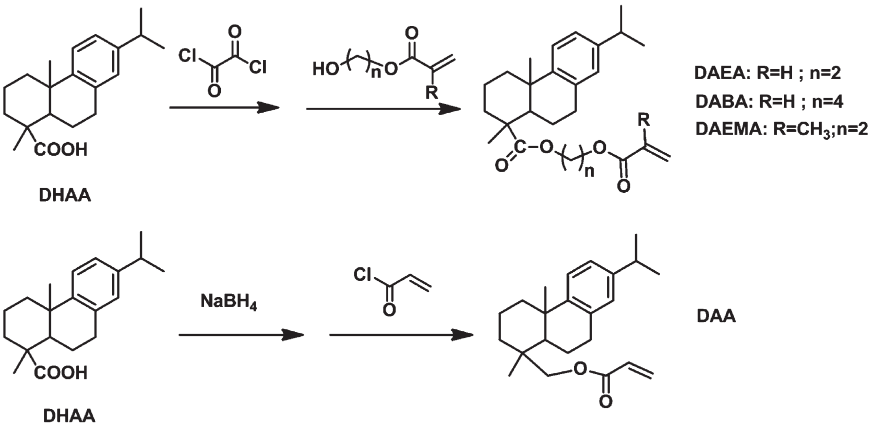

Table 1. ATRP of Vinyl Monomers Derived from Gum Rosin[a]

run	monomer	[M]/[I]/[C]/[L]	solvent	ligand	time (h)	conv (%)	M_n (NMR)	M_n (GPC)	M_w/M_n
1	DAA	100/1/0.5/0.5	THF	Me_6Tren	24	30	10 200	5 600	3.65
2	DAEA	100/1/0.5/0.5	THF	Me_6Tren	16	29	11 500	4 300	1.20
3	DABA	100/1/0.5/0.5	THF	Me_6Tren	16	54	21 500	7 700	1.25
4	DAEMA	100/1/0.5/0.5	THF	Me_6Tren	24	80	32 900	36 000	1.60
5	DAEMA	100/1/0.5/0.5	Anisole	Me_6Tren	20	75	31 000	19 000	1.33

[a] Initiator: ethyl 2-bromoisobutyrate; catalyst: CuBr; ligand: Me_6Tren; [M]/[I]/[C]/[L]: molar concentration ratio of monomer/initiator/catalyst/ligand; M_n(GPC): molecular weight obtained from GPC using PSt as standards; M_n(NMR): molecular weight obtained from ^{1}H NMR. Me_6Tren = tris[2-(dimethylamino)ethyl]amine; THF = tetrahydrofuran.

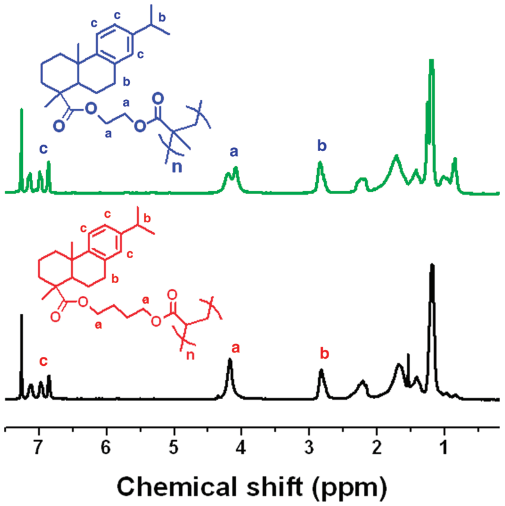

Figure 3. ^{1}H NMR spectra of PDABA and PDAEMA prepared by ATRP (corresponding to runs 3 and 5 from Table 1, respectively).

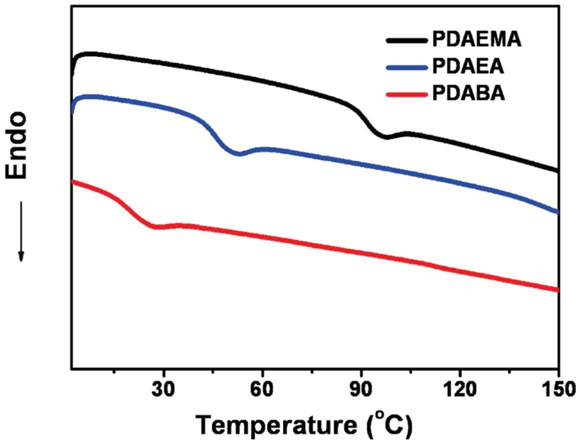

Figure 4. DSC traces of PDAEA, PDABA, and PDAEMA prepared by ATRP (corresponding to runs 2, 3, and 5 from Table 1, respectively).

The first stage exhibited a slight weight loss with similar onsets at 220 °C, although PDAEA showed noticeable higher loss (~15 wt %) than that of PDABA and PDAEMA (~5 wt %). TGA traces of the second stage were similar to onsets at nearly 325 °C followed by almost complete weight loss due to full decomposition of polymer backbones.

In conclusion, we have developed a strategy to synthesize a new class of monomers and well-defined renewable polymers from abundant low-cost natural resources: gum rosin. Highly pure rosin-derived acrylate and methacrylate monomers were prepared through simple esterification with dehydroabietic acid. The first well-defined rosin-derived polymers with low polydispersity and controlled molecular weight were obtained using ATRP. These polymers exhibited tunable thermal properties (e.g., glass transition temperature) by simple manipulation of monomer structures. The successful synthesis of rosin-derived monomers and well-defined polymers opens a new avenue toward development of a variety of rosin-derived renewable polymeric materials (e.g., thermoplastic elastomers, hybrids, composites) as potential competing replacement for petroleum-derived plastics.

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Supporting Information Available: Experimental details, GC-MS data, 2D-COSY ^{1}H NMR spectra, GPC data, and TGA traces of polymers (Figures S1−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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