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Synthesis and Thermal Properties of Hydrogenated Poly(styrene-*co*-1,1-diphenylethylene) Copolymers

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Introduction

Catalytic hydrogenation is an efficient way to enhance the chemical stability and glass transition temperature (T_g) of many unsaturated polymers. Catalytic hydrogenation of poly(diene)-based polymers has been practiced commercially since 1972.[1] Recent advances in catalytic hydrogenation chemistry have made the saturation of aromatic-containing polymers a commercially viable process.[2] We demonstrated previously that poly(styrene-*co*-α-methylstyrene) copolymers can be saturated using supported Pt or Pt/Re catalysts to produce novel polyolefins with T_g values up to 178 °C.[3]

1,1-Diphenylethylene (DPE) can be copolymerized anionically with styrene to form poly(styrene-*co*-1,1-diphenylethylene) (S/DPE) copolymers with T_g values as high as 175 °C.[4,5] Significantly, Knoll and co-workers recently reported that the DPE monomer can be produced by a low-cost process.[6] In this note, we describe the preparation and complete catalytic hydrogenation of S/DPE copolymers as sketched in Figure 1. The product, hydrogenated poly(styrene-*co*-1,1-diphenylethylene) (h-S/DPE), exhibits T_g values as high as 199 °C. These materials complement an expanding portfolio of high-temperature hydrocarbon plastics available for use in homopolymer or block copolymer forms.

Experimental Section

DPE (Aldrich) was purified by passing the monomer over activated alumina under flowing argon. Purification methods for styrene monomer and solvent were described in a previous paper.[3] The polymerizations were conducted in a dry 1 L glass reactor at reaction conditions listed in Table 1. For sample S/DPE-3 cyclohexane (150 mL), tetrahydrofuran (THF, 11 mL), and 14.2 g of DPE/cyclohexane solution (5.56 g DPE at 0.0309 mol) were added to the reactor. After the reaction temperature reached 30 °C, *sec*-butyllithium initiator (Aldrich, 0.21 mL, 0.27 mmol) was injected into the reactor. Styrene monomer (7.98 g, 0.0767 mol) was then added quickly to the reactor. This sequence of monomer addition ensures against rapid reaction prior to addition of the second monomer since DPE does not homopolymerize. After 6 h, degassed methanol was injected to terminate the reaction. Samples S/DPE-1 and S/DPE-2 were prepared similarly but without THF, which necessitated a higher polymerization temperature.

This synthetic procedure relies on disparate reactivity ratios for styrene and DPE. In particular, DPE will not homopolymerize under the conditions employed due to steric constraints,[4] while polystyryllithium reacts preferentially with DPE. Therefore, copolymerization of these monomers results in a distribution of repeat units that converges on perfectly alternating in the limit of stoichiometric addition, i.e., 50 mol % of each in the product polymer.

Precipitated and dried polymers were redissolved in cyclohexane at a concentration of 2 g/50 mL. Hydrogenations were conducted in a 0.1 L autoclave in the presence of a Pt−Re/SiO_2 porous catalyst (Dow Chemical) at a loading of 0.2 g catalyst per gram of polymer. Reactions were carried out with 500 psi H_2 pressure at 170 °C for 6 h. Hydrogenated polymers were precipitated in a 3:1 (v/v) methanol−2-propanol mixture and then vacuum-dried at 80 °C.

GPC traces were obtained using a Waters 717 Plus Autosampler equipped with three 5 μm mixed porosity Polymer Labs C columns and a Waters 410 differential refractive index detector at room temperature with THF as the mobile phase. The instrument was calibrated with polystyrene standards. ^{1}H NMR (Varian INOVA 300) was performed on polymer dissolved in $CDCl_3$.

Differential scanning calorimetry (DSC) results were obtained using a Perkin-Elmer DSC 7. Multiple heating and cooling scans were generated over a temperature range of 80−230 °C using a scan rate of 10 °C/min with nitrogen as the purge gas. Thermal degradation traces were acquired on a Perkin-Elmer TGA 7. Samples were heated from room temperature to 500 °C at a rate of 10 °C/min under a constant flow of N_2 (20 mL/min). Selected density measurements were obtained using calibrated density gradient columns.

Results and Discussion

Two sets of polymerization conditions were employed in producing the three S/DPE copolymers identified in Table 1, with and without THF. This polar modifier enhances the reaction kinetics permitting polymerization at lower temperature, resulting in a reduced polydispersity index. Similar copolymer compositions were obtained under both conditions, and in all three reactions nearly all the styrene monomer was consumed. Under ideal reaction conditions a perfect alternating copolymer of S and DPE, containing 63 wt % DPE repeat units, could be prepared. The highest of DPE incorporation obtained in this study was 50 wt %. Reducing the ratio of S to DPE should push the level of DPE incorporation toward the theoretical limit. Significantly, the overall copolymer compositions determined by NMR were similar to the initial monomer compositions, $f_{DPE}/F_{DPE} = 1.08$ (SDPE-1 and SDPE-3) and 1.24 (SDPE-2), where f_{DPE} is the mole fraction of DPE monomer charged to the reactor and F_{DPE} represents the mole fraction of DPE repeat units in the final polymer. This result, combined with the inability of DPE to homopolymerize, constrains the S and DPE repeat units to be relatively uniformly distributed within each copolymer.

All three S/DPE copolymers were catalytically hydrogenated, and the extent of saturation was determined by ^{1}H NMR. Greater than 98% saturation was achieved in each case. Figure 2 gives representative GPC traces for S/DPE-2 before and after hydrogenation. The shapes of the two peaks are nearly identical, indicating absence of chain degradation during the hydrogenation reaction.

Characterization results for the S/DPE and h-S/DPE specimens are listed in Tables 1 and 2, while Figure 3 presents representative DSC traces for samples before and after hydrogenation. T_g values for the h-S/DPE copolymers are plotted as a function of weight percent of hydrogenated DPE repeat units (h-DPE wt %) in Figure 4. Correlations between T_g and composition for the unsaturated and saturated materials can be approximated by

$$T_g = 1.09(\text{DPE wt \%}) + 100$$

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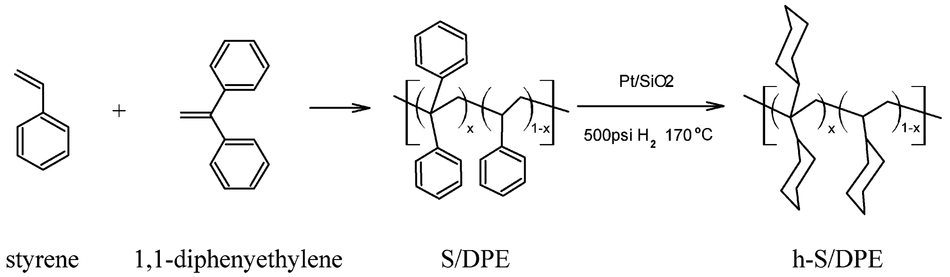

Figure 1. Synthesis scheme for the preparation of hydrogenated poly(styrene-*co*-1,1-diphenylethylene) (h-S/DPE) copolymer. *x* denotes the mole percent of 1,1-diphenylethylene (or hydrogenated 1,1-diphenylethylene) units in the copolymer.

Table 1. Polymerization Conditions and Properties of S/DPE Copolymers

samples	M_n,[a] kg/mol	PDI[a]	DPE,[b] wt %	[Li], mmol/L	[THF], mol/L	[DPE], mol/L	[S], mol/L	temp, °C	reaction time, h	DPE yield, %	T_g, °C
S/DPE-1	27	1.32	35	1.03	0	0.11	0.31	68	6	97	132
S/DPE-2	20	1.44	50	0.95	0	0.17	0.20	66	6	70	154
S/DPE-3	41	1.10	38	1.37	0.62	0.15	0.38	30	6	95	146

[a] From GPC, using PS standards. [b] Measured by ^{1}H NMR.

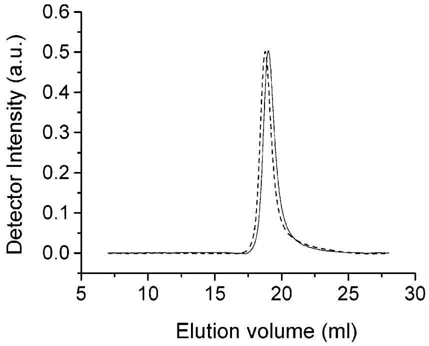

Figure 2. GPC traces of S/DPE-1 (dashed line, before hydrogenation) and h-S/DPE-1 (solid line, after hydrogenation). These traces confirm the absence of chain degradation during hydrogenation.

Table 2. Properties of Hydrogenated S/DPE Copolymers

samples	h-DPE, wt %	h-DPE, mol %	M_n,[a] kg/mol	PDI[a]	T_g, °C	density,[b] g/cm^3
h-S/DPE-1	35	24	26	1.28	177	
h-S/DPE-2	50	37	20	1.37	199	
h-S/DPE-3	38	26	40	1.08	184	0.962

[a] Polydispersity index from GPC, based on PS standards. [b] Measured at 25 °C.

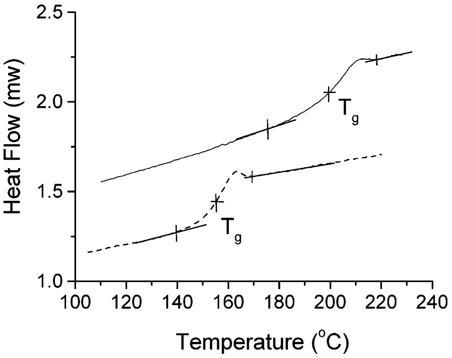

Figure 3. DSC traces obtained from the S/DPE-2 (dashed line) and h-S/DPE-2 (solid line) copolymers.

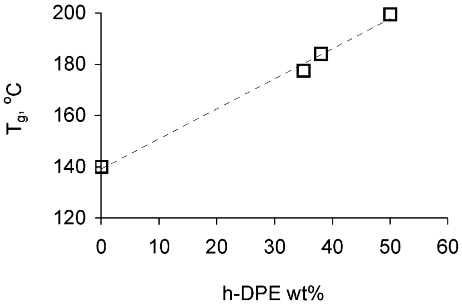

Figure 4. T_g values obtained for h-S/DPE (open square) as a function of the wt % of hydrogenated DPE (h-DPE) repeat units. The dashed line is a linear fitting to these data.

and

$$T_g = 1.17(\text{h-DPE wt \%}) + 100$$

in degrees centigrade. The DPE wt % dependence is slightly lower than that previously reported by Knoll et al.,[6] who found that the T_g of S/DPE increases by 1.26 °C/wt % DPE. This small difference (0.17 °C/wt %) might result from the smaller molecular weights employed here or possibly a different segment sequence distribution. Comparison of the thermal analysis results before and after hydrogenation reveals that on average saturation leads to a 40–45 °C increase in T_g. This T_g increase also will be affected by the detailed distribution of repeat units that result from the polymerization kinetics. Characterization of segment distribution by high-resolution NMR is outside the scope of this brief note. Nevertheless, the width of the glass transition for S/DPE-2 (Figure 3), which is only moderately broader than that of a typical random copolymer, is consistent with a relatively homogeneous distribution of styrene and diphenylethylene repeat units. (The low-temperature tail in the DSC curve for h-S/DPE-2 is puzzling but cannot reflect additional broadening of the repeat unit sequencing which is not affected by hydrogenation.)

Hydrogenation also leads to a sizable decrease in density, from 1.076 g/cm^3 for S/DPE-3 to 0.962 g/cm^3 for h-S/DPE-3, both at 25 °C. This change is nearly identical to that associated with the hydrogenation of poly(styrene).[7] The hydrogenated materials exhibit thermal degradation characteristics similar to those of PS, with only 0.5% weight loss recorded by TGA at 290 °C.

In the event that DPE can be manufactured at or near commodity prices, this compound represents an attractive addition to the compliment of hydrocarbon monomers (e.g., butadiene, isoprene, styrene, α-methylstyrene) that can be catalytically hydrogenated following polymerization. An attractive and potentially useful range of upper use temperatures, $T_{g,PCHE} \cong 140-148$ °C,[7] $T_{g,PCEP} \cong 140-178$ °C,[3] and $T_{g,\ h-S/DPE} \cong 140-200$ °C, now can be incorporated into block architectures using established synthetic procedures.[3]

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References and Notes

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