

Design of Polymers for Migration Imaging Applications. I. Copolymerization of *p*-Decylstyrene

INTRODUCTION

Photographic migration imaging is a novel imaging technique involving the preferential movement of amorphous selenium particles within a softenable polymeric matrix. The basic process has been described by Goffe,¹ the sensitometry and mechanism have been studied by Pundasack² and Tutihasi,³ and the image fixing and abrasion resistance studied by Buckley and co-workers.⁴

In material studies involving migration imaging polymers, both polymer softening point and composition were thought to be important. After the optimum softening point has been determined, it is desirable to vary composition at constant softening point. To carry out such studies, it was desirable to have four monomers available. Two monomers must yield homopolymers having very low softening points, while two monomers must yield homopolymers having high softening points. Each monomer pair must consist of one polar and one nonpolar monomer.

The Fox equation⁵ can be used to estimate the softening point or T_g of terpolymers knowing the T_g or softening point of each corresponding homopolymer and the desired fraction of each monomer unit in the terpolymer. In this way, polymer softening point and polarity can be varied systematically using combination of these four monomers.

Polar monomers were available. Poly(methylmethacrylate) has a T_g of 105°C, while poly(laurylmethacrylate) has a T_g of -65°C. On the nonpolar side, polystyrene has a T_g of 100°C; however, no readily available styrene derivative was found with a comparatively low polymer T_g . Polydiene materials were not considered suitable because of residual unsaturation in the polymer. A perusal of the literature indicated that a *p*-alkylstyrene would give a low polymer softening point or T_g and be nonpolar.

For poly(*p*-alkylstyrenes) the relationship between T_g and the length of the alkyl chain is known.⁶ As the alkyl chain is lengthened, the T_g decreases until at the decyl analog interchain forces lead to a progressive increase in T_g as the chain is further lengthened.

On this basis the decyl analog, *p*-decylstyrene was chosen since that monomer gave the lowest polymer T_g in the series and the starting material, decylbenzene, was readily available. In addition, its synthesis, described very generally by Overberger and co-workers,⁶ appeared free of serious experimental difficulties.

This communication describes an improved synthesis of *p*-decylstyrene and its copolymerization behavior with styrene and methyl methacrylate.

EXPERIMENTAL

Preparation of 4-Decylacetophenone

n-Decylbenzene (2050 g) and nitromethane (3000 g) were mixed in a 22-liter flask. With vigorous stirring, aluminum chloride (7 lb, anhydrous) was added quickly. Acetic anhydride (1375 g) was added to this slurry at a rate of about 50 g/min. The exothermic reaction was cooled externally, then allowed to reflux. The last 5% addition should cause no noticeable exotherm. After stirring 30–60 min, the reaction mixture was hydrolyzed by the addition of about 12–24 liters of ice.

The reaction was steam distilled to remove the nitromethane. The organic layer was separated from the distillation residue and washed well with water, then dilute sodium bicarbonate solution, and then water, until the extract was neutral to pH paper. The organic layer was separated, dried over sodium sulfate, and distilled. The product boiled at 166–168°C at 1.5 mm Hg. A 90% yield was typical. The literature⁶ boiling point was 166–8/1.5 mm.

Preparation of 4-Decylphenylmethylcarbinol

Lithium aluminum hydride (16 g) was dissolved in 200 ml anhydrous ether in a 3-liter flask mounted with a stirrer, condenser, and addition funnel. 4-Decylacetophenone (200 g) dissolved in 800 ml anhydrous ether was added at about 30 ml/min. The reaction was exothermic and con-

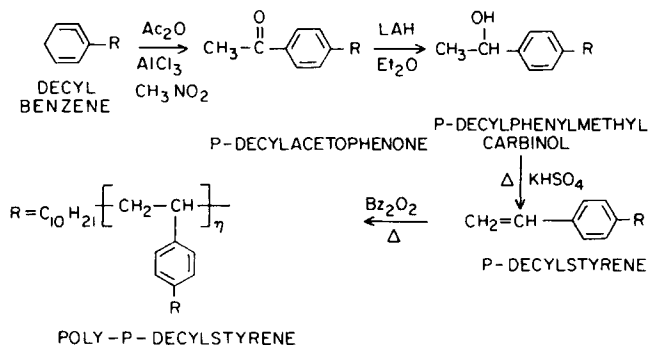


Fig. 1. Schematic diagram for the preparation of poly(*p*-decylstyrene).

trolled by external cooling. After 30 min of additional stirring, the excess hydride was destroyed by the slow addition of ethyl acetate (150 ml). The reaction mixture was hydrolyzed by the careful addition of 1000 ml 10% hydrochloric acid. Good stirring was essential during this step.

The organic layer thus formed was separated. The aqueous layer was extracted with 500 ml ether to extract additional product. The ether layers were combined and dried over anhydrous sodium sulfate. The drying agent was filtered off and the ether distilled, yielding a residual oil which crystallized on standing.

The residual oil may be distilled, bp 153°C at 1 mm Hg, or recrystallized from 30–60°C petroleum ether, using a 20% solution in petroleum ether cooled in acetone–Dry Ice. This material has mp 41–42°C. The yield was near quantitative. The literature⁶ melting point was 39–40°C.

Preparation of 4-Decylstyrene

A 500-ml, three-neck flask was fitted with a thermometer extending to near the flask bottom, a steam-heated addition funnel, and a constant-reflux, variable-takeoff stillhead. Fused potassium acid sulfate (1 g/25 g carbinol) was added to the flask. The vacuum was regulated at about 20 mm Hg using a manostat, and the flask was heated using a Woods metal bath such that the internal temperature was 190°C. The corresponding bath temperature was about 230°C. A portion of 4-decylphenylmethylcarbinol (25–50 g) was added. After several minutes, the dehydration began and water began to distill. After the completion of the water distillation, the vacuum was increased (2–7 mm Hg) and the product began to distill. After completion of product distillation, another batch of carbinol was added and the procedure was repeated.

After the dehydration was completed, the organic distillate was separated from the water, dried, and distilled (bp 140°C at 1 mm Hg or 150–155°C at 7 mm Hg). The literature⁶ boiling point was 139–143°C at 1 mm. The yield varied between 50% and 85%.

DISCUSSION

Preparation of *p*-Decylstyrene Monomer

p-Decylstyrene was synthesized in two steps from readily available decylbenzene, as shown in Figure 1. The procedures used were those general procedures referenced by Overberger.⁶ For convenience, the reduction was carried out using lithium aluminum hydride.

The acetylation of decylbenzene was carried out by previous workers in carbon disulfide. This solvent was considered too hazardous for large-scale lab work, and nitromethane was substituted.

Reaction temperature was studied using gas chromatography to separate the product isomers. At room temperature the reaction yielded a product which gave a gas chromatogram composed of a peak with a pronounced shoulder. Product obtained from reactions run at 0°C show only a single peak with no evidence of a shoulder. On this basis a reaction temperature of 0°C was chosen. The infrared spectrum of this material had a CH out-of-plane deformation at 830 cm⁻¹, indicating predominately para substitution. A strong conjugated carbonyl absorption occurred at 1680 cm⁻¹. The NMR spectrum showed a quartet centered at 462 cps. The splitting was typical of symmetrically substituted aromatics. The yield of acetylated decylbenzene was 100% of crude material by gas chromatographic analysis. Only minimal losses occurred during work-up.

Reduction of *p*-decylacetophenone to the carbinol proceeded smoothly using lithium aluminum hydride in ether. The yield was 91% of a material whose mp 40–41°C was a good agreement with a literature⁶ value of 39–40°C. Gas-chromatographic analysis of the carbinol indicated purity greater than 99%. The infrared spectrum was consistent with the structure of an aromatic carbinol having a hydroxyl absorption at 3320 cm⁻¹ and the typical aromatic absorptions.

Dehydration of the carbinol was carried out using fused potassium acid sulfate at 230–240°C and 5 mm Hg. The yield of monomer was 70%. It was assayed by gas-chromatographic analysis and was shown to be at least 99% pure. The infrared and NMR spectrum of the monomer was consistent with the structure. The observed boiling point was identical to that reported previously.⁶

Preparation of *p*-Decylstyrene Copolymers

Copolymers of *p*-decylstyrene were synthesized to obtain specific softening points for the copolymers and also to widely vary the amount of methacrylate in the polymer. Polymerizations were initiated thermally, and most proceeded to high conversions in convenient times. The ratio of total monomer to solvent was 1 to 3. The conversion was determined by gas-chromatographic analysis of unreacted monomers.

In Table I these *p*-decylstyrene copolymers are characterized in terms of composition, softening point, and intrinsic viscosity. Composition was determined by elemental analysis and nuclear magnetic resonance spectroscopy. Agreement was excellent between the two methods. There was more divergence in the methods when low-melting polymers were involved. This is reasonable because of the greater problems in purification of polymers softening below room temperature. At higher molecular weights (runs B, D, and F), as estimated by intrinsic viscosity measurements, the softening range was reasonably close to the predicted T_g from the Fox equation differing by about 3–4°C. Styrene/*p*-decylstyrene copolymers were synthesized having softening points varying from 86° to 52°C.

The data in Table I show that nonpolar polymers with softening ranges significantly less than 100°C can be synthesized. Copolymers of *p*-decylstyrene and methyl methacrylate were also synthesized with softening ranges from 100°C to softening below room temperature using copolymer compositions from 10/90 to 80/20. Agreement of softening point to predicted T_g using the Fox equation was not good and may have been due to low molecular weight in some cases.

TABLE I
Physical Properties of *p*-Decylstyrene Copolymers

Run designation	Monomer ^b	Feed ratio	Composition ^a			T_g from Fox eq., ^b	Intrinsic viscosity (toluene, 30°C)
			Elemental analysis	NMR	Soft range, °C		
A	STY/PDS	90/10	89%	91	85–103°C	91	0.21
B	STY/PDS	90/10	90	90	86–122	91	0.55
C	STY/PDS	85/15	87	85	65–86	87	0.28
D	STY/PDS	85/15	83	84	83–110	84	0.52
E	STY/PDS	80/20	82	80	52–76	83	0.26
F	STY/PDS	80/20	80	80	77–99	81	0.57
G	PDS/MMA	80/20	97	—	25	-57	—
H	PDS/MMA	20/80	25	—	46–64	81	—
I	PDS/MMA	10/90	14	—	100–127	92	—

^a % Composition refers to first monomer in column 2 in mole-%.

^b STY = Styrene; PDS = *p*-decylstyrene; MMA = methyl methacrylate.

TABLE II
Monomer Reactivity Ratios for the Systems *p*-Decylstyrene/Styrene and *p*-Decylstyrene/Methyl Methacrylate in Tetralin at 200°C

M_1	M_2	r_1	r_2	$r_1 r_2$
<i>p</i> -Decylstyrene	styrene	1.05 ± 0.17	1.07 ± 0.15	1.12
<i>p</i> -Decylstyrene	methyl methacrylate	0.88 ± 0.23	1.47 ± 0.38	1.29

p-Decylstyrene Reactivity Ratios

Gas-chromatographic analysis was used to study quantitatively the copolymerization behavior of *p*-decylstyrene with styrene and methyl methacrylate to relatively high conversions by determination of the monomer reactivity ratios using the integrated copolymer equation of Mayo and Lewis⁷ as modified by Harwood and co-workers.⁸

Monomer reactivity ratios for the copolymerization of *p*-decylstyrene with styrene and with methyl methacrylate are described in Table II. The polymerizations were carried out in tetralin at 200°C.

Styrene and *p*-decylstyrene copolymerize in an almost ideal fashion which is not unexpected in view of the molecular similarities and previous studies⁹ of the styrene/*p*-vinylbiphenyl system. *p*-Decylstyrene copolymerizes with methyl methacrylate, with the *p*-decylstyrene rate lower than that of methyl methacrylate at 200°C.

In summary, *p*-decylstyrene has been synthesized and copolymerized with styrene and with methyl methacrylate and the copolymers characterized. The monomer reactivity ratios of *p*-decylstyrene with styrene and methyl methacrylate were determined.

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