

High-Temperature Thermoplastic Elastomers via the Grafting Reaction of Polyarylate onto EPDM Rubber

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SYNOPSIS

Polyarylate monofunctionally terminated with a 1,2-dihydrobenzocyclobutene group undergoes thermally initiated grafting reactions onto ethylene/propylene/nonconjugated diene rubber via the Diels–Alder reaction between the diene (benzocyclobutene) and the dienophile (pendant unsaturation on the EPDM). Characterization of the graft copolymer(s) is presented as is the resultant thermoplastic elastomeric mechanical performance exhibited by the graft copolymers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The synthesis of well-defined graft copolymers has long been a challenge to the polymer chemist. Traditional routes to graft copolymers involving rubbers requires functionalizing the rubber or reacting the rubber such that monomer units are polymerized in the presence of the rubber to form random graft copolymers. In the case of EPDM rubber, peroxide-mediated polymerization of vinyl monomers results in both graft copolymer and nongrafted homopolymer.^{1,2} A more elegant and efficient methodology involves the macromonomer approach, whereby a polymer functionally terminated with a reactive “monomer” is polymerized into the elastomer backbone.^{3,4} High-temperature hard-segment graft copolymers, i.e., EPDM-*g*-polypivalolactone, have also been prepared by anionic polymerization of pivalolactone in the presence of a carboxylated EPDM rubber.^{5,6} A high-impact polystyrene has been made by reacting a benzocyclobutene-modified styrene/*N*-arylmaleimide copolymer with EPDM rubber.⁷

The use of 1,2-dihydrobenzocyclobutene functionality in polymer synthesis was pioneered concurrently by Tan and Arnold⁸ and Kirchhoff et al.^{9–11} with the focus being high-temperature thermosetting resins for composite applications.

Similar approaches have been applied to amorphous engineering thermoplastics and uncured rub-

bers via functionalization with the 1,2-dihydrobenzocyclobutene followed by thermal curing to obtain thermoset polymeric materials.¹²

This paper will discuss research in our laboratory on the synthesis of high-performance thermoplastic elastomers derived from EPDM rubber and polyarylate hard segments via 1,2-dihydrobenzocyclobutene (referred to as benzocyclobutene) Diels–Alder chemistry.

EXPERIMENTAL

Preparation of 1,2-Dihydro-4-Chloroformylbenzocyclobutene

3-Bromo-4-(2-chloroethyl)benzoic acid (26.3 g) was dissolved in 200 mL of tetrahydrofuran distilled from sodium ribbon. The solution was cooled to -100°C with a liquid nitrogen bath and tertiary butyl lithium (75 mL of 2.7 *M* in pentane) was added under nitrogen via a syringe over a 10 min period. The reaction solution (bright orange) was held at -80°C for 30 min, then allowed to warm to room temperature over 2.5 h. The reaction was quenched with 5 mL of 5% aqueous hydrochloric acid. The tetrahydrofuran solution was diluted with 350 mL of pentane, resulting in a white precipitate. The precipitate was filtered, washed thoroughly with water, and recrystallized from a water/ethanol mixture (80/20). A white, crystallized solid (13.6 g), 92.1% yield with a melting point of $87\text{--}88.5^{\circ}\text{C}$, was recovered.

$^1\text{H-NMR}$ (CD_3CN , δ) 3.12 (4H, s), 7.27 (1H, d), 7.89 (1H, d), 7.93 (1h, S), 11.4 (1H, s, D_2O exchangeable). $^{13}\text{C-NMR}$ (CD_3CN , δ) 29.31, 29.43, 122.51, 125.72, 136.72, 137.81, 146.62, 146.73, 172.61.

ANAL: Calcd: C, 72.96%; H, 5.44%.

Found: C, 72.87%; H, 5.41%.

The carboxylic acid was converted to the corresponding acid chloride by refluxing (neat) the 1,2-dihydrobenzocyclobutene-4-carboxylic acid (13.6 g) with 15.3 g (1.4 equiv) of thionyl chloride for 4.5 h. Excess thionyl chloride was removed by vacuum-distillation, resulting in a waxy, solid product. The acid chloride can either be used directly without further purification or distilled under vacuum (bp 62.5–63.5°C/5 mm) to give a water-white liquid that slowly solidifies (mp = 42–43.5°C).

ANAL: Calcd: C, 64.88%; H, 4.24%; Cl, 21.28%.

Found: C, 64.87%; H, 4.22%; Cl, 21.31%.

Preparation of Polyarylate

A 250 mL round-bottom flask equipped with a 316 SS motor-driven stirrer, a thermocouple, and a Barret trap topped with a water condenser was charged with 200 g (0.601 mol) of phenyl- α -(*p*-hydroxyphenyl) cumate and 0.02 mol % of lithium phenoxide. The reaction mass was heated to 280°C with a fluidized sand bath under vacuum (aid in the removal of phenol). After 6 h at 280°C, a water-white, highly viscous melt was obtained. The polymer was removed from the flask and ground to a nominal 100 mesh particle size. The polymer had an inherent viscosity (IV) of 0.23 dL/g in 60/40 phenol/1,1,2,2-tetrachloroethane.

The molecular weight of the prepolymer was readily advanced using a Brabender torque rheometer with a single-screw devolatilizing attachment having a 25 L/D. Using 310°C temperature profile, molecular weight was controlled by residence time and vacuum level to achieve IV's of 0.23 to 0.81 dL/g.

End Capping of Polyarylate with 1,2-Dihydro-4-Chloroformylbenzocyclobutene

A 1 L round-bottom flask equipped with a glass paddle motor-driven stirrer was charged with 60 g of polyarylate (desired IV, Table I), 5 g of 1,2-dihydro-4-chloroformylbenzocyclobutene, and 600 mL of dichloromethane. Once dissolved, 4 drops of triethylamine was added and the reaction stirred under nitrogen at 30°C for 12 h. The polymer was recovered (and freed from the unreacted end-capping agent) by repeated coagulation into isopropanol using a Waring blender.

EPDM-g-Polyarylate Copolymer Preparation

A Brabender mixing apparatus was charged with a specified quantity of benzocyclobutene end-capped polyarylate and a specified quantity of EPDM rubber at 220°C. The mixing bowl temperature was raised to 265°C and held for 5 min at 100 rpm. For the entire time, the polymers were purged with nitrogen. At the end of the 5 min mixing time, the dark orange, transparent mass was removed and compression-molded into a 4 × 4 × 0.020 in. sheet. One 8-in. strip was shear cut from the molded sheet for physical property measurement.

Analytical Techniques

Gel Permeation Chromatography: The data were obtained on a Hewlett Package 701 LFJ-R dual detector instrument equipped with a medium pressure mercury vapor lamp with a FJ-436X filter (for 436 mm absorption).

Polyarylate end-capped with benzocyclobutene was dissolved in distilled diphenylether under nitrogen. *N*-Naphthacenemalimide was added to the polyarylate solution (1/1 w/w based on polyarylate). The polyarylate solution was heated to reflux for 5 h, cooled to 25°C, diluted with dichloromethane

Table I End-group Characterization

Polyarylate	IV (dL/g) ^a	Phenolic OH ($\mu\text{eg/g}$) ^b	BCB End Cap ($\mu\text{eg/g}$) ^c	GPC Ratio [Eq. (3)]
A	0.23	122	127	0.998
B	0.39	72	74	1.012
C	0.60	51	52	1.009
D	0.81	23	24	1.005

^a Inherent viscosity in phenol/TCE (60/40 W/W) at 25°C.

^b Potentiometric titration.

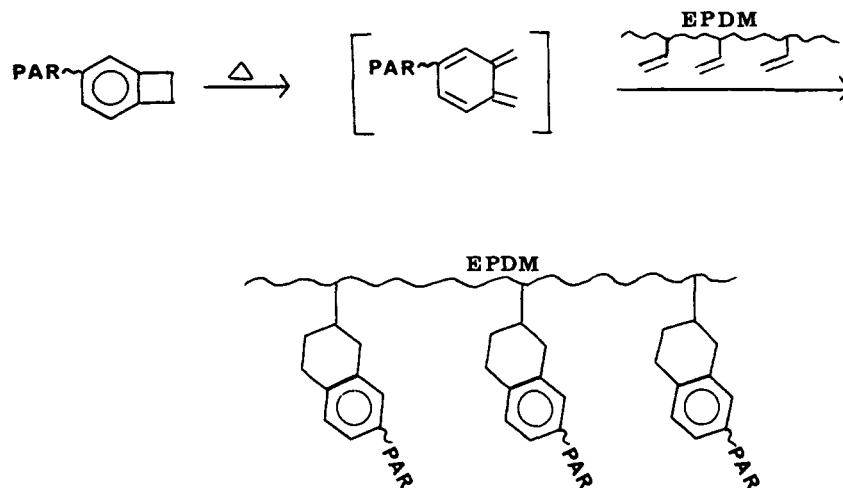
^c Proton NMR (3.17 δ resonance).

to 5% solids, and the polyarylate recovered by coagulation into methanol. The polyarylate bearing the naphthacene tag will be used to define the benzocyclobutene functionality per polymer chain (see Results and Discussion).

RESULTS AND DISCUSSION

Achieving a well-defined EPDM-*g*-polyarylate copolymer requires a chemistry that effects a high

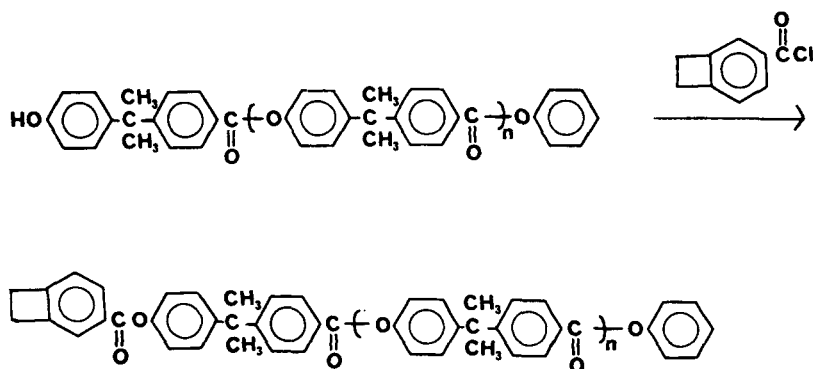
grafting efficiency that is not reversible or subject to side reactions at high temperatures. End capping a polyarylate with a benzocyclobutene functionality provides a reactive group that will undergo a thermally allowed electrocyclic ring opening to an *o*-quinodimethane, i.e., a diene. Activation of the benzocyclobutene group in the presence of an EPDM rubber bearing pendant carbon-carbon double bonds results in a $4 + 2 \pi$ allowed reaction resulting in a graft point [eq. (1)]:



The ring-forming reaction between the pendant unsaturation on the EPDM and *o*-quinodimethane end group results in an aromatic ring adduct; hence, it is thermally irreversible. The relatively high energy of activation (39.9 kcal/mol) for the benzocyclobutene ring opening does, in fact, require tempera-

tures of 250–270°C for the process to proceed on a reasonable time scale.¹³

The polyarylate used in this study [eq. (2)] was synthesized from an AB monomer condensation reaction resulting in phenolic hydroxy end groups and phenylester end groups:



The end capping of the polyarylate was carried out in a postpolymerization step where 1,2-dihydro-4-chloroformylbenzocyclobutene was reacted by a Schotten-Baumann process, thereby maximizing

monofunctionalization of available polyarylate chains.

To confirm the monofunctional nature of the end capping with the benzocyclobutene, two techniques

were employed. First, the polyarylate prior to functionalization was analyzed by potentiometric titration for hydroxyl end groups, and then after functionalization, for benzocyclobutene functionality by proton NMR (methylene resonance 3.17 δ). The data in Table I support that all hydroxyl end groups were reacted during the functionalization step. However, all that these data determine is that all hydroxyl end groups were capped with the benzocyclobutene group; they do not address whether all polyarylate chains are monofunctional with respect to the benzocyclobutene end group.

Even though the polyarylate is derived from an AB monomer, this does not guarantee all chains to be functionalized. Using a dynamic gel permeation chromatography technique pioneered by Kennedy and Smith,¹⁴ a dual visible/refractive index analysis of each polyarylate sample was evaluated. The visible detector on the GPC was tuned to 436 nm—the absorption (ϵ max = 29,400) for aminonaphthacene. The aminonaphthacene tag was introduced by reacting the maleimide derivative with the available benzocyclobutene end cap. The assumption is that all benzocyclobutene groups react with the maleimide derivative since a fivefold molar excess of maleimide was used based on NMR quantification.

The dual visible/refractive index sampling of each polyarylate chain passing through the GPC columns allows for a comparison of a ratio of the heights of the response curves for $(\text{VIS}/\text{RI})_x$ at a given elution volume vs. $(\text{VIS}/\text{RI})_y$ for all elution volumes plotted against the corresponding molecular weight values: $(\text{MW})_y$ vs. $(\text{MW})_x$. Thus, if all polyarylate chains are monofunctionally end-capped with the benzocyclobutene group, then

$$\left[\frac{(\text{VIS}/\text{RI})_x / (\text{VIS}/\text{RI})_y}{(\text{MW})_y / (\text{MW})_x} \right] = 1.0 \quad (3)$$

The data in Table I shows that virtually all polyarylate chains are capped with a single benzocyclobutene group.

With quantified benzocyclobutene functionality in hand, the grafting reaction was developed. Using Nordel® EPDM rubber (E. I. DuPont) having 4.7% 1,4-hexadiene as the nonconjugated diene component, i.e., the dienophile in the grafting reaction, a series of EPDM-*g*-polyarylates were prepared. By varying both the IV and the weight percent of polyarylate graft, a wide range of physical properties is achievable (Table II). The graft copolymers exhibit balanced thermoplastic elastomer performance across the compositional variation at the two different polyarylate (hard segment) IVs. Within a hard segment IV series, mechanical property performance increases with increasing level of polyarylate graft content.

The thermoplastic character of the graft copolymers is demonstrated based on the melt flow index data as all copolymers could be extruded to give dark orange, transparent strands with good surface character. In addition, all extruded strands were soluble in monochlorobenzene, i.e., no covalent cross-links. The ability to thermally process the graft copolymers is consistent with the solubility parameter difference for EPDM ($17.2 \text{ J}^{1/2}/\text{cm}^{3/2}$) and the polyarylate ($19.0 \text{ J}^{1/2}/\text{cm}^{3/2}$) as calculated.¹⁵ The dynamic mechanical thermal analysis (DMTA, Fig. 1) demonstrates good phase separation between the hard-segment polyarylate graft and the soft-segment EPDM backbone.

In summary, benzocyclobutene monofunctionally terminated polyarylate can be reacted with elastomers bearing pendant dienophile character, e.g., EPDM to generate EPDM-*g*-polyarylate copolymers. The graft copolymers exhibit good thermoplastic elastomer mechanical performance.

Table II EPDM-*g*-Polyarylate Thermoplastic Elastomer Properties

Polyarylate (wt %)	15	35	50	—	—	—
B	15	35	50	—	—	—
C	—	—	—	15	35	50
EPDM (wt %)	85	65	50	85	65	50
T_g ($^{\circ}\text{C}$, DSC)	-35,201	-55,201	-55,201	-55,205	-55,205	-55,205
MFI ^a	47.1	34.2	30.1	27.2	20.1	14.7
Tensile strength (psi)	2,010	3,400	4,800	2,580	4,700	5,910
Tensile modulus (kpsi)	18.1	32.4	54.3	20.2	40.6	62.3
Elongation at break (%)	162	225	470	272	422	520
Compression set (%)						
25 $^{\circ}\text{C}$	29	17	10	21	5	4
100 $^{\circ}\text{C}$	39	22	17	34	11	9

^a Melt flow index at 300 $^{\circ}\text{C}$ 1P.

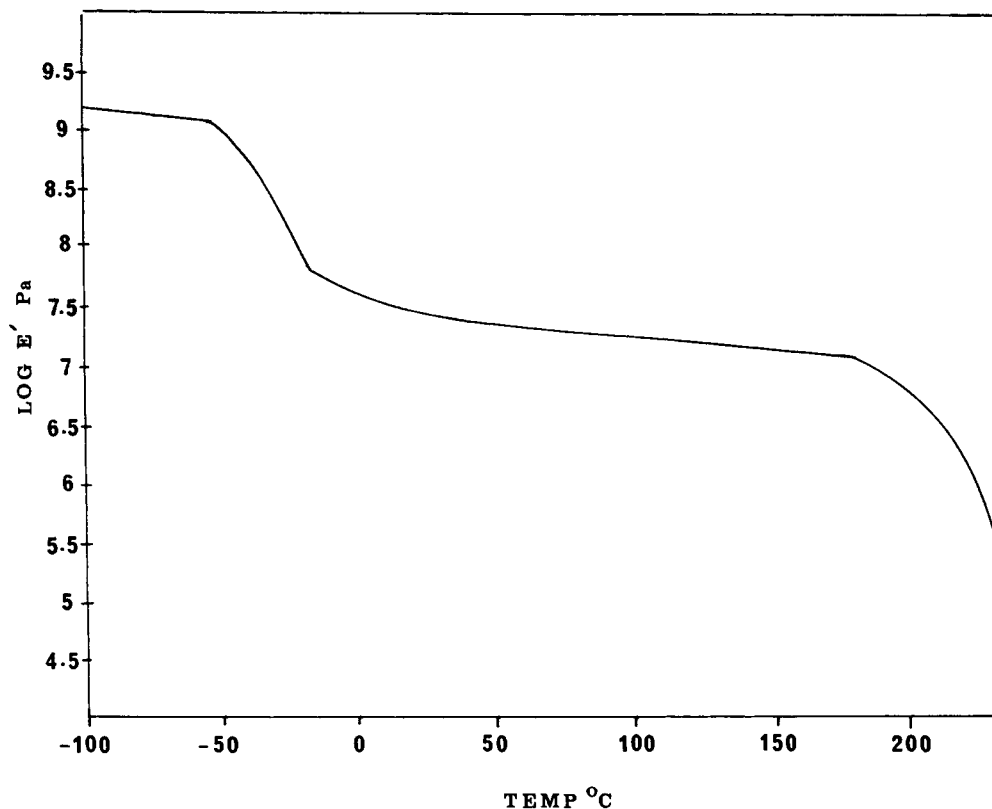


Figure 1 EPDM-g-Polyarylate C (50/50).

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