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Nanodispersion of Polybutadiene in Polystyrene through Controlled "Grafting from" Free Radical Polymerization Using a Diphenylmethyl Type Radical

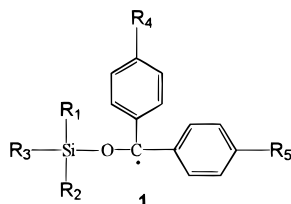
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Following recent advances in free radical polymerization, we developed a controlled route to graft polystyrene on polybutadiene (PB) which overcomes the lack of selectivity of primary free radicals found during the traditional preparation of high impact polystyrene or HIPS.¹ In this new approach two stages are included. In the first one, the PB or butadiene copolymers are reacted with diphenylmethyl type stable free radicals **1** to form thermoreversible bonds^{2,3} and in the second,



the modified rubbers are used as free radical initiators⁴ in a *grafting from* reaction displaying the characteristics of a *controlled* free radical polymerization. Thus, the PB-**1** bonds can be thermally cleaved during the polymerization to produce two free radicals with distinctly different reactivities toward styrene: the polybutadienyl radical and **1**.

The polybutadienyl radical acts as initiator, while the stable free radical **1** acts as the molecular weight controller disturbing the normal termination by reversible end capping of the growing chains (see Scheme 1). The inclusion of this reaction in the global termination rate term (disproportionation and coupling), R_t , provide living characteristics to the polymerization. But, distinct from stable free radicals as TEMPO, its effect is only observed at low conversions.⁵ Moreover, in accord with controlled-polymerization definition,⁶ we have proved that in styrene polymerizations initiated by **1** (where $R_1 = R_2 = R_3 = \text{CH}_3$ and $R_4 = R_5 = \text{H}$), the average molecular weight increases with conversion.⁷ Consequently, the molecular weight of grafts reached under the controlled regime is also low. This means that after a threshold value of conversion, the suppression of the primary termination by **1** fall off because of the occurrence of irreversible termination between chains, consumption of **1** in secondary reactions, and self-polymerization. It is important to note that self-polymerization rate at 110 °C is 9%/h.

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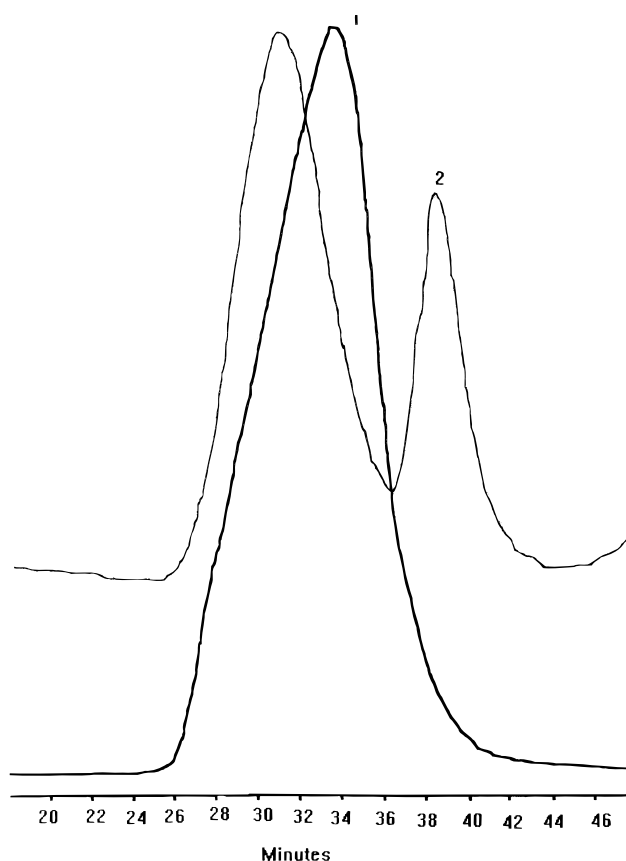


Figure 1. SEC curves for graft copolymer S-21 (**2**) initiated by modified rubber E1502 (**1**) whose average functionality, F , was calculated to be 0.9.

Under this context, it is reasonable to anticipate that the formation of PB-*graft*-PS is carried out during the controlled regime in which the formation of networks is fairly limited. Indeed, the early presence of this species in the medium brings about changes on the evolution of phase patterns. The miscibility of phases polystyrene-styrene/polybutadiene-styrene is improved as a result of efficient grafting, reducing the ability of PB coils to agglomerate in phases. Consequently formation of nanometrical PB phases stabilized by the grafted polystyrene chains can be expected.

Graft copolymerizations were performed first in bulk in sealed tubes without agitation and afterward in toluene in a 400 mL jacketed reactor at 110–120 °C. Whatever the case, the concentration of PB was chosen to be 7% with respect to styrene and the polymerization was stopped at values of conversion largely exceeding those reached by initiated-polymerization through **1**, i.e. 23–73%.

After polymerization, the products were isolated by precipitation to determinate conversion and percent of gel. Translucent films were prepared by casting; iridescence was observed during the evaporation of toluene. Nacreous surfaces and the Tyndall effect was observed in dry films, indicating the presence of particles with very small sizes. Results of experiments carried out with three different elastomers are quoted in Table 1.

In Figure 1, we can observe the overlay of SEC traces of both the functional PB macroinitiator E1502 and the

Scheme 1

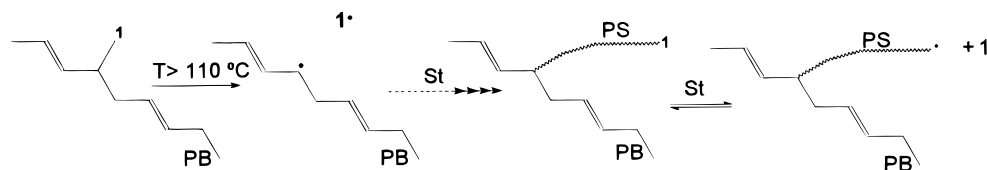


Table 1. Results of Graft Polymerization Initiated Three Different Modified Elastomers

graft copolymer	elastomer initiator	styrene conversion (%)	gel (%)	film transmittance (0.3 mm) (%)	rubber content ^c (%)	$M_n \times 10^{-3}$ (g/mol)
S-21 ^a	E1502	23	37	78	21.0	151
S-21R ^b	E1502	71	5	35	5.7	165
S-22 ^a	S255P	26	49	61	12.9	116
S-22R ^b	S255P	72	4	55	7.1	174
S-23 ^a	Buna	45	27	9	31.3	102
S-23R ^b	Buna	73	8	56	8.0	175

^a Carried out in solution. ^b Carried out in sealed tubes. ^c In soluble fraction.

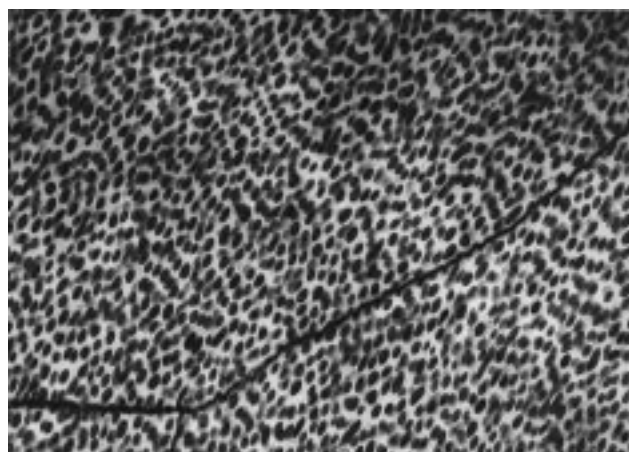


Figure 2. TEM micrograph of ultrathin section of a cast films of S-21 stained with OsO_4 ($2.7 \text{ cm} = 1 \mu\text{m}$). Photo reduced 50% for publication.

graft copolymer S-21, which shows that the peak of the copolymer is shifted to higher molecular weight. This result clearly indicates the high efficiency of the grafting reaction. On the other hand, the peak at low molecular weight (16 000) was identified by a diode-array detector to be polystyrene which was probably initiated by **1**.

Thin sections from casted films were obtained at -80°C using a cryoultramicrotome and deposited on carbon-coated electron microscopy grids. They were subsequently stained with OsO_4 and observed by transmission electron microscopy. Thermodynamically controlled morphologies obtained from cast films are observed in the micrograph shown in Figure 2, which reveals the presence of well-dispersed submicron particles with a narrow size distribution and no visible subinclusions. The stability of PB phases can be explained by the presence of surrounding demixed grafted polystyrene chains which are immersed in polystyrene matrix. In this micrograph we can also observe a dark line which was produced by a long thermal treatment of the sample at temperatures above T_g of PS.

The above technique constitutes a simple method for the nanodispersion of PB in polystyrene to produce translucent and gloss materials having interesting morphologies. Although chain-breaking reactions can happen during the growth of grafted chains, the number of the side chains can be easily controlled by adjusting

the ratio PB/**1**.² Mechanical properties of obtained nanocomposites are currently under study.

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References and Notes

- (1) Fisher, M.; Hellmann, G. P. *Macromolecules* **1996**, *29*, 2498–2509.
- (2) In this first stage, the reaction is carried out by dissolving a known ratio between PB and an appropriate generator (TPSE) of free radicals **1** in toluene, and then the solution is refluxed for 1–2 h. Under these conditions, the production of stable radicals is extremely high, which provokes the accumulation of species **1** in the medium. The concentration of this radical decreases slowly as the PB is being modified. After 1–2 h, the color developed by the free radicals vanishes and the reaction is stopped. The product is then precipitated, filtered, dried, and analyzed to determinate the average number of **1** attached to PB according to the equation $F = m(\text{DP}_n/100)$, where m is the mole percent of **1** in PB as determined by comparing the peak areas of polybutadiene double bonds ($\delta = 5.0\text{--}5.6 \text{ ppm}$) and those of the trialkylsilyloxy group ($\delta = 0 \text{ ppm}$) in the ^1H NMR spectra. The efficiency F of this reaction can be obtained from m and the initial amount of TPSE. In all cases, the calculated F was close to 10%.
- (3) Some of these radicals were previously reported by others authors. See for example: Braun, D.; Steinhauer-Beiber, S. *Eur. Polym. J.* **1997**, *33*, 7–12 and references cited herein.
- (4) During the second stage, the thermoreversible bonds are easily cleaved to produce graft copolymers. The reactions were performed by dissolving 7% of modified PB in styrene with or without toluene and heating at $110\text{--}120^\circ\text{C}$ for 3–7 h. Styrene conversion and gel percent were calculated gravimetrically. In both cases, iridescence was observed during the polymerization and transparent blue-sky-like films were obtained by cast.
- (5) Guerrero-Santos, R.; De León Sáenz, M. E.; Y. Gnanou *Polym. Prepr.* **1997**, *38* (1), 667–668.
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