Letters

Preparation of polydiene-g-polystyrene graft copolymers

There are several reports of the preparation of graft copolymers via the reaction of monofunctional prepolymers with suitable polymer backbones[1–8]. In all but one of these reports the reactive prepolymer is a living polymeric carbanion or cation which cannot be isolated. In the one example where the prepolymer is capable of isolation (amino-terminated polystyrene) the grafting reaction was achieved with a specially prepared methyl methacrylate copolymer having pendant isocyanate groups[8].

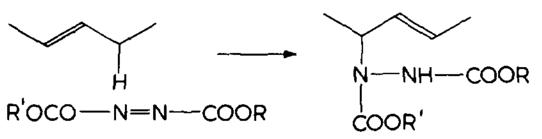
We report here a new type of grafting process in which one reactant is a stable monofunctional styrene prepolymer, capable of being isolated and handled in the atmosphere, and the other reactant is an unmodified polydiene. The ability of the prepolymer to form a graft junction at any repeat unit of the polydiene is a considerable advantage over grafting processes which rely on previous chemical modification of the backbone because of the increased effective concentration of one of the reactants in the grafting process.

The coupling reaction for graft copolymer formation is based on the 'ene' addition of azodicarboxylates to allylic double bond systems (equation 1)[9]. Polystyrene with an azodicarboxylate functional group at one end only of the polymeric chain can be synthesized by the sequence of reactions shown in equation 2. The starting point is polystyryl lithium formed by anionic polymerization of styrene in cyclohexane initiated with n-butyllithium in the presence of *N,N,N′N′*-tetramethylethylenediamine.

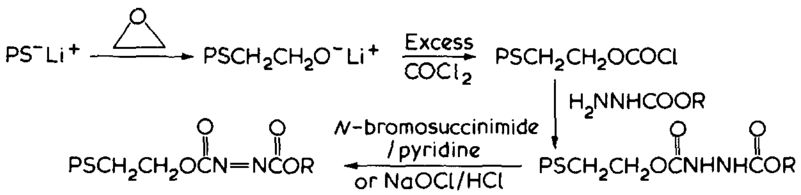
Samples of polystyrene prepolymers are isolated after termination with ethylene oxide and characterized for molecular weight and molecular weight distribution by g.p.c. analysis. Alkoxide (hydroxyl) functionality is estimated by silylation with a mixture of trimethylchlorosilane and hexamethyldisilazane in pyridine solution[10] followed by silicon analysis by atomic absorption spectroscopy. At this stage the polymer functionality based on $\bar{M}_n$ from g.p.c. and silicon content is >90%. Characterization of the azodicarboxylate-terminated polystyrene is less rigorous because of a lack of a universally applicable procedure for quantitative estimation of the azodicarboxylate functional group. G.p.c. analysis demonstrates that polymer coupling can be kept very low (<3%) during the synthetic sequence and infra-red spectra (dichloromethane solution) provide semiquantitative characterization of the hydrazodicarboxylate and azodicarboxylate polymers (hydrazodicarboxylate carbonyl 1740 cm^{-1}, >NH 3400 cm^{-1}; azodicarboxylate carbonyl 1785 cm^{-1}). The azodicarboxylate function shows a weak but characteristic absorption at 407 nm ($\epsilon = 34$, by analogy with model compounds) which is readily detected in dichloromethane solutions of the azodicarboxylate-terminated polystyrenes at molecular weights ($\bar{M}_n$) < 10 000. The normal polystyrene absorption does not interfere significantly at this wavelength but the oxidation conditions for conversion of hydrazodicarboxylate to azodicarboxylate result in a low wavelength absorption tail which interferes with the azodicarboxylate absorption at 407 nm and in many cases invalidates the use of this absorption maximum for quantitative analysis.

The azodicarboxylate-terminated polystyrenes are isolated by precipitation into alcohol and are stable for prolonged periods as dry powders. Reaction with polydiene backbones occurs in cyclohexane solution at 60°C over a period of days and infra-red spectra of the reaction products indicate that essentially all the azodicarboxylate function is consumed. G.p.c. analysis of the total reaction product with u.v. detection at 262 nm (polystyrene only) shows some free polystyrene prepolymer but the majority of the response is associated with a peak of much higher molecular weight. Similar analysis with detection at 215 nm (polystyrene and polydiene) again shows the peak due to some free polystyrene prepolymer and the higher molecular weight peak, with enhanced response of the latter due to the contribution of polydiene. The distributions of the high molecular weight peaks under detection at 215 and 262 nm are identical within experimental error indicating that uniform grafting of the polydiene chains has occurred.

Grafting efficiencies can be calculated from the areas of the peaks in the g.p.c. analysis (detection at 262 nm) and are reported in *Table 1*. The efficiencies are expressed as the percentage of the total polystyrene which becomes bound to the polydiene. The ungrafted polystyrene includes all prepolymer which, for one reason or another, had failed to acquire the azodicarboxylate functional group during the synthetic sequence. The overall grafting efficiencies can be high. We believe that for reaction with Cariflex IR305 synthetic polyisoprene they are virtually quantitative when based on the azodicarboxylate content of the polystyrene prepolymer but require further evidence to support this view. The grafting efficiencies for natural rubber (NR) reflect some deleterious influence of non-rubber constituents. However, the reactions were



(1)



$$PS^-Li^+ \xrightarrow{\text{ethylene oxide}} PSCH_2CH_2O^-Li^+ \xrightarrow[COCl_2]{\text{Excess}} PSCH_2CH_2OCOCl \xrightarrow{H_2NNHCOOR} PSCH_2CH_2O\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}OR \xrightarrow[\text{or } NaOCl/HCl]{N\text{-bromosuccinimide}/\text{pyridine}} PSCH_2CH_2O\overset{O}{\overset{\|}{C}}N{=}N\overset{O}{\overset{\|}{C}}OR$$

(2)

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Table 1 Grafting of azodicarboxylate-terminated polystyrenes on polydiene backbones

Polystyrene			Backbone polymer	Grafting efficiency (%)
$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	Content (wt %)		
5450	1.11	40	IR[b]	73
8900	1.11	40	IR	77
		20	IR	78
17 700	1.12	40	IR	67
8900	1.11	40	NR[c]	57
		20	NR	49
5450	1.11	40	BR[d]	63

[a] Not corrected for column broadening; [b] synthetic polyisoprene, Cariflex IR305; [c] natural rubber, SMR5L; [d] polybutadiene, Intene 55NF

performed on commercial grades with no prior purification. Extraction of the NR before reaction results in grafting efficiencies comparable to those obtained with Cariflex IR305.

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Crossover from the dilute to the semidilute regime as determined from n.m.r. of poly(ethylene oxide) chains

Introduction

The purpose of this Letter is to suggest that suitable nuclear magnetic relaxation (n.m.r.) properties observed on flexible polymer chain solutions can be used to determine the point where a crossover has been predicted to occur by increasing the concentration from the dilute regime to the semidilute[1].

It is known that in the dilute regime the volume $V_G \approx R_G^3$ of an isolated chain is a function of molecular weight, M (R_G is the radius of gyration: $R_G^2 \propto M^{6/5}$) but is independent of concentration[2]. A concentration crossover line $C^*(M,T)$ to the semidilute regime has been predicted from recent descriptions of polymer–solvent systems based on analogous properties of magnetic systems considered in the critical domain[1,3]. C^* is considered as the concentration $C^* \simeq NV_G^{-1}$ of overlap of polymer chains (N is the number of monomer units). At concentrations higher than C^* overlapping chains are entangled and polymer solutions must exhibit a correlation length, ξ, such that $\xi^2 \propto C^{-3/2}$; ξ is independent of molecular weight. The concentration crossover occurs at the point where $\xi(C^*) = R_G$.

The entanglement concept[4] and the above description are reconciled by identifying ξ with the average distance between two consecutive chain coupling junctions or entanglements[5]. A spatial crossover induced by concentration or temperature variations has been recently well observed from neutron scattering experiments performed on polystyrene chain solutions[6]. The Fourier transform of the pair correlation function of monomer units exhibits a crossover length q^{*-1}. More recently, a determination of C^* has been proposed using ultra-violet spectroscopy as a technique to probe monomer unit environment[7].

Transverse magnetization correlation function

Properties of the correlation function of the transverse magnetization associated with nuclear spins bound to polymer chains in solutions have been extensively studied on polyisobutylene[8–10]. By analysing experimental results two concentration ranges can clearly be distinguished. One of these (I) spreads from the pure polymer state to a concentration C_i; the other one spreads from C_i to infinite dilution.

(i) It has been well established that the n.m.r. response observed on high molecular weight ($\approx 10^6$) polyisobutylene chain solutions in the concentration range (I) exhibits solid-like and liquid-like character. The solid-like character is clearly reflected either by a high resolution spectrum narrowing effect induced by sample rotation[9] or by a pseudo-solid spin echo whose amplitude goes to zero upon chain dilution[11]. This response is related to a residual dipolar spin coupling which is supposed to result from monomer unit non-isotropic motions induced by the presence of entanglements. It is also observed on *cis*-1,4-polybutadiene[11] and poly(dimethyl siloxane)[12] chains.

On the other hand, the spectrum narrowing effect is not observed on polymer chain solutions in the concentration range (II); in highly dilute solutions chains are free to rotate and no residual dipolar spin coupling can be observed.

(ii) Also, it has been shown that the linewidth Δ observed on polyisobutylene chain solutions in the concentration range (I) exhibits a characteristic dependence upon solvent concentration and temperature; Δ^{-1} is a linear function of $\gamma = \nu_1(1-\nu_1)^{-1}$ (ν_1 is the molar fraction of solvent); Δ reflects the probability of association of two monomer units taking the free energy of

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