

Graft copolymers from azodicarboxylate-functional pre-polymers: 1. Synthesis of azodicarboxylate-functional polystyrene

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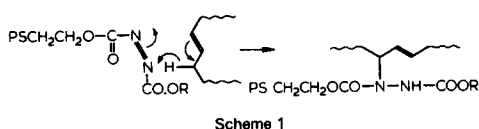
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A synthetic sequence is described for the preparation of polystyrenes in the molecular weight range (\bar{M}_n) 3×10^3 to 2×10^4 having terminal azodicarboxylate functionality with one functional group per polymer chain. The polymer end groups are characterized spectroscopically at each step in the synthetic sequence. The concentration of azodicarboxylate groups on the polymers is determined spectroscopically and compared with the \bar{M}_n of the polymers as calculated from initiator/monomer ratio or as measured by g.p.c. analysis.

(Keywords: polystyrene; end groups; hydroxyl; chloroformate; hydrazine-1,2-dicarboxylate; azodicarboxylate)

INTRODUCTION

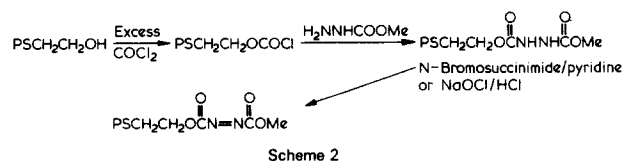
Two preliminary communications from our Laboratory^{1,2} have defined a novel approach to the formation of poly(diene-*g*-styrene) graft copolymers using a principle of chemical reaction between pre-formed constituents. The graft copolymer product is formed by cycloaddition of azodicarboxylate functionality on the polystyrene component to the allylic double bond system of polydiene backbones:



The chemistry of the cycloaddition reaction is well documented³ and the reaction has been applied to crosslink formation in diene rubbers⁴ and to chemical modification of diene rubbers with relatively low molecular weight chemical groups^{5,6}. The orientation of the addition, as represented in Scheme 1 is arbitrary; attachment to the polydiene chain may occur through the other nitrogen atom of the azo group. Use of the cycloaddition reaction in graft copolymer formation is a logical extension of previous rubber modification chemistry. The present paper will describe the synthesis of azodicarboxylate-functional polystyrenes. Subsequent publications will discuss the grafting reactions and the properties of the graft products in some detail.

Graft copolymer formation by the reaction shown in Scheme 1 potentially offers a degree of control over side chain content and side chain molecular weight which is not accessible from free radical grafting reactions. In order to utilize this potential to the full, synthesis of the required

azodicarboxylate-functional polystyrene has been aimed at obtaining high polymer functionality with specifically terminal location of the functional group and with complete exclusion of polystyrene molecules carrying more than a single functional group. The latter criterion was considered important because multi-functionality would give rise to the unwanted complication of gel formation during the grafting reactions. Anionic polymerization of styrene, reaction of the carbanion with ethylene oxide and protonation of the polymer alkoxide is a recognized reaction sequence for preparation of hydroxyl-functional polystyrene of very high and specifically terminal hydroxyl functionality⁷ and if initiation is via a butyl lithium species the polymer is monofunctional. Such a hydroxyl-functional polymer is the starting point for the sequence of reactions in Scheme 2 for synthesis of the azodicarboxylate function. The reaction steps of Scheme 2 are well documented in organic chemistry and will be discussed in this paper only in the specific context of reactions on the polystyrene end group.



EXPERIMENTAL

Materials

Argon (BOC, zero grade) was purified through two traps containing solutions of living polystyrene in decalin. Cyclohexane (May and Baker, commercial grade) was flash distilled, stirred over 20% oleum for 16 h to remove unsaturated material, stirred over sodium bicarbonate

Table 1 Molecular weight data for hydroxyl-functional polystyrenes

Polymer	\bar{M}_n , (predicted) ^a	\bar{M}_n , (g.p.c.)	<i>d</i> ^b
A	3 800	3 200	1.07
B	6 000	5 500	1.11
C	7 600	8 200	1.06
D	9 300	8 900	1.11
E	10 800	12 700	1.04
F	20 000	17 700	1.12

^a From nominal initiator concentration and monomer weight^b Uncorrected for column broadening

slurry and dried over magnesium sulphate. It was then passed through basic alumina (2.51/150 g) and stored over 3 Å molecular sieve. Immediately before each polymerization, the cyclohexane was refluxed over calcium hydride for 2 h under purified argon and distilled directly into the polymerization vessel. Styrene (Koch Light, puriss grade) was stored over calcium hydride and distilled from fresh calcium hydride *in vacuo* immediately before use. The vacuum was broken with purified argon and the receiver sealed with a rubber septum. *n*-Butyl lithium was a 1.6 M solution in hexane (Aldrich Chemical Co.). The solution was transferred under purified argon pressure to a storage vessel fitted with a double entrance port which could be purged with argon before the solution was sampled with a hypodermic syringe. The arrangement gave more reliable multiple sampling of a single batch of solution than direct use of the syringe needle on the bottle septum. *N,N,N',N'*-tetramethylethylenediamine (TMEDA, Aldrich Chemical Co.) was dried over calcium hydride and purified by bulb-to-bulb distillation *in vacuo*. It was stored in an argon atmosphere in a refrigerator. Ethylene oxide (BOC Special Gases) was freed from protic impurities by contact with a small amount of *n*-butyl lithium solution in cyclohexane. Tetrahydrofuran and dichloromethane were redistilled under nitrogen before use. All other reagents were used as purchased.

Synthetic procedure

Glassware for the polymerization reaction was dried *in vacuo* at 80°C for several hours before use and thoroughly purged with purified argon. The polymerization vessel was a 3 l single neck flask fitted with a 4 mm bore tap adaptor. A side-arm above the tap allowed the space outside the tap bore to be flushed with argon while the tap was open for solution manipulations. The synthetic procedure is given in some detail for polymer D.

Cyclohexane (1.5 l) was distilled into the polymerization flask. *n*-Butyl lithium solution (28 ml, nominally 0.045 moles) and TMEDA (5.6 ml, 0.042 moles) were syringed into the flask and the solution was cooled in an ice bath until approximately half of the cyclohexane had crystallized to form a slurry. Freshly distilled styrene (416 g) was transferred to the stirred slurry rapidly via a glass delivery tube, using argon pressure and the polymerization was allowed to proceed in the stirred solution. The reaction exotherm melted the cyclohexane and brought the solution close to boiling point within minutes. The ice bath was retained around the reaction vessel and gas pressure was allowed to vent back through the glass delivery tube to the monomer vessel and thence

to the atmosphere. The reactions were controllable under the specified conditions but any increase in scale is not recommended using this procedure. The polymer solution was stirred at room temperature overnight in a closed argon atmosphere. Ethylene oxide (6 ml, 0.12 moles) in cyclohexane solution was transferred to the polymer solution using argon pressure and caused immediate discharge of the deep red polymer carbanion colour. The hydroxyl-functional polymer was recovered by precipitation into industrial methylated spirits (IMS; 95% ethanol) (10 l) containing concentrated Analar hydrochloric acid (10 ml), and was dried *in vacuo* at 50°C.

Dried hydroxyl-functional polymer (423 g, 0.0475 moles based on g.p.c. \bar{M}_n) was dissolved in freshly distilled tetrahydrofuran (1.5 l) and the solution was added dropwise to liquid phosgene (100 ml, 1.4 moles) at -10° to 0°C over 4 h. The reaction was stirred continuously and the apparatus was protected with a cold trap at -78°C and sodium hydroxide traps. The reaction solution was purged with nitrogen overnight and the residual phosgene was removed by distillation of solvent (250 ml). Triethylamine (8 ml, 0.085 moles) and methyl carbazate (7.2 g, 0.08 moles) were added and the solution was stirred at room temperature for 18 h then heated under reflux for 2 h. The hydrazinedicarboxylate polymer was recovered by precipitation into IMS (10 l) and dried *in vacuo* at 50°C. The dried polymer (414 g) was dissolved in dichloromethane (1.5 l). Pyridine (4.2 ml, 0.052 moles) and *N*-bromosuccinimide (8.3 g, 0.047 moles) were added and the solution was stirred at room temperature overnight. The solution was washed with hydrochloric acid (1 M, 2 × 500 ml), saturated aqueous sodium hydrogen carbonate (2 × 500 ml) and water (2 × 500 ml) and the polymer was recovered by precipitation into IMS (10 l) and dried *in vacuo* at room temperature. Infra-red spectroscopy indicated the presence of hydrazinedicarboxylate function in the product as well as the expected azodicarboxylate. The oxidation sequence was repeated using one third of the original oxidant quantities to give the product characterized in Table 2.

Two preparations (polymers B and F) followed an alternative procedure which reduced the number of polymer isolation steps. The procedure for polymer B was as follows. The cyclohexane solution of hydroxyl-functional polymer was evaporated to a gum (approximately 60% solids) which was then diluted with dichloromethane (1 l). The solution was added dropwise to phosgene (100 g) at 0°C over 6 h and the mixture was kept at 10°C overnight. Excess phosgene was removed by co-distillation with dichloromethane and the solvent was replenished with more dry dichloromethane. Methyl carbazate (30 g, 0.33 moles) was added and the polymer solution was heated at 35°C for 3 h, kept at room temperature overnight and again heated at 35°C for a further 2 h. Concentrated hydrochloric acid (20 ml, 0.22 moles) was added and the solution was filtered through diatomaceous earth to remove insoluble hydrochlorides. More hydrochloric acid (10 ml) was added and sodium hypochlorite solution (1.03 M, 90 ml) was added dropwise over 2.5 h. The solution was kept in a closed flask overnight and the polymer was recovered by precipitation into IMS.

Polymer characterization

Infra-red and ultra-violet spectra were recorded on

Table 2 End group analysis data for functional polystyrenes

Polymer	[Polymer chains] ^a (mol g ⁻¹ × 10 ⁴)	[OH groups] ^b (mol g ⁻¹ × 10 ⁴)	[Azo groups] ^c (mol g ⁻¹ × 10 ⁴)	Azo functionality (%)	Grafting ^d efficiency (%)	Coupled ^e polymer (%)
A	2.63	2.39	2.10	76	79	3.6
B	1.67	1.68	1.26	71	74	5.9
C	1.32	1.17	0.95	68	72	2.1
D	1.08	1.00	0.84	74	77	1.6
E	0.93	0.82	0.67	68	63	—
F	0.50	0.51	—	—	68	8.4

^a Reciprocal of \bar{M}_n predicted from nominal initiator to monomer ratio

^b From silicon content of silylated polymers

^c From u.v. spectra

^d Average values from several grafting experiments

^e From g.p.c. analysis

Perkin Elmer 157 and 402 spectrometers respectively, using solutions of polymer in chloroform (10% w/v). Cell path lengths were 0.5 mm and 10 mm respectively. Gel permeation chromatograms were obtained in tetrahydrofuran solution (0.025% w/v) at a flow rate of 1 ml/min on five PL Gel columns (Polymer Laboratories; nominal pore sizes 10⁶, 10⁵, 10⁴, and 5 × 10² Å) using a Perkin Elmer PE601 pump and LC55 ultra-violet detector operating at 215 nm. Molecular weight calibration used a set of narrow distribution polystyrene standards (Polymer Laboratories) having molecular weights in the range 2 × 10³ to 100 × 10³.

Silylation of hydroxyl-functional polymer used the reagent mixture described by Sweeley *et al.*⁸. The reagent solution was prepared from hexamethyldisilazane (5 ml) and chlorotrimethyl silane (2.5 ml) in dry pyridine (12.5 ml). Hydroxyl-functional polymer (0.5 to 1.0 g) was dissolved in dry pyridine (5 ml) and allowed to react with silylation reagent (0.5 ml) at room temperature for 2 h. The solution was evaporated to dryness under reduced pressure. The residue was dissolved in toluene and the evaporation and dissolution repeated twice. The toluene solution was then centrifuged to remove insoluble material and evaporated to dryness and the residue was powdered and dried *in vacuo* at 60°C for 48 h. The silicon contents of the silylated polymers were determined by atomic absorption using a Varian 1200 atomic absorption spectrometer. The polymer was metered directly as a solution in toluene (10 mg/ml). The repetitive evaporation sequence was used to remove excess reagents and silylated low molecular weight impurities in preference to polymer reprecipitation, in order to avoid the possibility of polymer fractionation at the lower polymer molecular weights.

RESULTS AND DISCUSSION

The conditions for the polymerization of styrene were similar to those used by Helary and Fontanille⁹ for kinetic measurements of the propagation of polystyryl carbanion in the presence of TMEDA, but using a higher carbanion concentration. The initiator was n-butyl lithium in the presence of approximately one molar equivalent of TMEDA. Cyclohexane was chosen as polymerization solvent in preference to toluene or benzene to avoid any possibility of carbanion transfer¹⁰. The polymer solutions remained homogeneous, although polystyrene has limited solubility in cyclohexane at room

temperature. The molecular weights (\bar{M}_n) of the hydroxyl-functional polymers, as measured by g.p.c. analysis, agreed with the molecular weights predicted from initiator/monomer ratio within the range ±16% (see Table 1). For two polymers (A and F) the g.p.c. molecular weights were more than 10% lower than the values calculated from the total titrable alkali in the n-butyl lithium initiator solution. This observation, together with further indirect evidence from end group analysis (*vide infra*) indicates that the predicted molecular weights (\bar{M}_n) from nominal initiator/monomer ratios may be more consistently accurate than the g.p.c. results. The molecular weight distributions (*d*) were narrow, indicating fast initiation by the n-butyl lithium-TMEDA complex even in the poorly solvating cyclohexane solvent.

Direct qualitative evidence for the presence of hydroxyl functionality on the polymers was given by an i.r. absorption peak at 3550 cm⁻¹. The absorption was weak but persisted after repeated evaporation of toluene solutions of the polymers to dryness and prolonged drying *in vacuo* at 60°C. A more quantitative assessment of hydroxyl functionality was given by silicon analysis of the silylated polymers (Table 2). The experimentally determined hydroxyl group concentrations were within the range 88 to 102% of the calculated polymer chain concentrations when the \bar{M}_n values from initiator to monomer ratio were used as a basis for comparison. The agreement was less satisfactory (77 to 104%) when the comparison was made using \bar{M}_n from g.p.c. measurement.

Two separate procedures for the conversion of hydroxyl-functional polymer to azodicarboxylate-functional polymer are described in the experimental section. Both follow the general chemical sequence of Scheme 2. For polymers A, C, D and E the hydroxyl-functional polymer was converted to polystyryl methyl hydrazine-1,2-dicarboxylate by consecutive reactions with phosgene and methyl carbazate in THF. The polymer chloroformate was not normally isolated, but for polymer A an i.r. spectrum was recorded in solution and a sample was dried to constant weight *in vacuo* for chlorine analysis. The i.r. spectrum showed a strong carbonyl absorption at 1780 cm⁻¹ characteristic of the chloroformate group. The chlorine content was equivalent to a chloroformate end group concentration of 3.01 × 10⁻⁴ mol g⁻¹, i.e. approximately 15% above the predicted end group concentration. The rate of addition of the hydroxyl-functional polymer to the phosgene must be controlled to prevent an accumulation of free hydroxyl

groups in the reaction solution and consequent reaction with polystyryl chloroformate to give di-(polystyryl) carbonate. Under the preparation conditions described this coupling reaction could be kept to an acceptably low level (*Table 2*). The levels of coupled polystyrene listed in *Table 2* were measured on the final azodicarboxylate-functional polymers but in a separate experiment (not listed) the polymer chloroformate was prepared under standard conditions in THF and reacted with excess ethanol. Analysis of the resultant polymer carbonate showed a coupled polymer content of 2.2%. The THF solutions of polymer chloroformate were reacted with methyl carbazate in the presence of triethylamine as hydrogen chloride scavenger. Chloroformates react with tertiary amines to give alkyl chloride and carbamate, or by decomposition of the chloroformate to alkyl chloride and carbon dioxide¹¹. For this reason the first preparation (Polymer A) was carried out with simultaneous dropwise addition of tertiary amine and carbazate to prevent a build-up of a high concentration of free tertiary amine. In subsequent preparations (polymers C, D and E) tertiary amine and carbazate were added together at the start of the reaction for reasons of experimental convenience and although the final azo functionalities of the latter polymers were lower, no direct confirmation was obtained that this decrease was a consequence of chloroformate decomposition.

THF is not an appropriate solvent for the oxidation of hydrazine-1,2-dicarboxylate groups to azodicarboxylate groups. Polymers A, C, D and E were, therefore, isolated as methyl polystyryl hydrazine-1,2-dicarboxylate prior to oxidation. Qualitative confirmation of the hydrazine dicarboxylate end group structure was obtained from i.r. and n.m.r. spectra (3400 cm^{-1} , $>\text{N-H}$; 1740 cm^{-1} , $-\text{NH-CO-OR}$; $3.8 \pm 0.05\text{ ppm}$ $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{NH-}$). The methyl ester signal in the n.m.r. spectrum could, in principle, be used for quantitative assessment of the hydrazine-1,2-dicarboxylate end group, using dibromomethane as an added standard but the signal was weak in all but the lowest molecular weight polymer and the precision was poor, even with the help of spectral accumulation techniques. The oxidation to azodicarboxylate-functional polymer was carried out in dichloromethane solution using *N*-bromosuccinimide in the presence of pyridine^{12,13}. Polymers C and D showed residual $>\text{N-H}$ absorption at 3400 cm^{-1} and a residual shoulder near 1740 cm^{-1} after the standard oxidation sequence. These polymers were re-treated with oxidation reagents to give the results reported in *Table 2*.

The preparation of polymers B and F followed an experimentally more convenient procedure which avoided intermediate isolation of solid polymer. Conversion from hydroxyl-functional polymer to azodicarboxylate-functional polymer in the polymerization solvent (cyclohexane) was impracticable because of low reagent solubilities and also because the extent of formation of di-(polystyryl) carbonate during reaction with phosgene became excessively large (up to 22%). An acceptable compromise was achieved by using dichloromethane for the phosgene, carbazate and oxidation reactions, although the extent of formation of coupled polystyrene increased significantly. The oxidation reagent for polymers B and F was nominally hypochlorous acid generated from sodium hypochlorite and hydrochloric acid. The procedure was more convenient than the use of

chlorine water¹⁴. Polymer F showed residual $>\text{NH}$ and hydrazinedicarboxylate carbonyl absorptions in the i.r. spectrum after the first treatment with oxidant and was re-oxidized to give the results shown in *Table 2*.

The oxidized polymers were isolated as yellow powders by precipitation into IMS. Contact time with the alcohol was kept short to minimize loss of azodicarboxylate-functionality by dehydrogenation reactions¹⁵. Subsequent experience has shown that the dehydrogenation is catalysed by acid and it is possible that the apparently incomplete oxidation of polymers C, D and F in the standard oxidation procedures was due to re-formation of hydrazinedicarboxylate from azodicarboxylate catalysed by residual free acid during precipitation.

The azodicarboxylate functional group was qualitatively identified by a strong carbonyl absorption at 1785 cm^{-1} in the i.r. spectra¹⁶ and by the methyl ester proton signal at 4.05 ppm in the n.m.r. spectra. The u.v. spectra of azodicarboxylates are reported in the literature. There is some disagreement over the value of the molar extinction coefficient for the absorption¹⁶⁻¹⁸, and there is also a strong dependence on solvent and some dependence on structure^{17,18}. We have found that the polymers show λ_{max} at 408 nm in chloroform and 405 nm in benzene in agreement with simple dialkyl azodicarboxylates and that the extinction coefficient ϵ , increases linearly with increasing benzene concentration in chloroform-benzene solvent mixtures. The magnitude of this increase corresponds to the magnitude observed for diethyl azodicarboxylate rather than for di-isopropyl azodicarboxylate. We have therefore adopted the extinction coefficient ($\epsilon = 40$) of diethyl azodicarboxylate in chloroform containing 10% v/v benzene as an appropriate value for the measurement of azo group concentration in 10% w/v solutions of the polymer in chloroform. The azo functionality of the polymers was defined as the azo group concentration expressed as a percentage of the predicted polymer chain concentration. The low value of the extinction coefficient resulted in a decrease in the accuracy of the measurement as the M_n increased beyond 10^4 . Polymers B and F (hypochlorous acid oxidation) and polymer E (*N*-bromosuccinimide oxidation) showed enhanced absorption below 400 nm relative to a spectrum of diethyl azodicarboxylate run in 10% v/v benzene in chloroform against chloroform reference. For polymer B, the contribution of the tail of this absorption to the azodicarboxylate absorption at 408 nm was negligible but for polymer E the contribution was more significant. For polymer F the absorption tail was sufficiently pronounced to obscure the weak azodicarboxylate maximum, although the i.r. spectrum confirmed the presence of azodicarboxylate end group. The u.v. spectra of the other polymers were free from enhanced short wavelength absorption.

The azodicarboxylate-functional polystyrenes reacted efficiently with unsaturated rubbers. The reactions will be discussed in detail in subsequent publications but the efficiency of grafting to Shell Cariflex IR-305 polyisoprene in cyclohexane solution is given in *Table 2* for each of the polymers described in this paper. At the lower molecular weights (polymers A, B, C and D) grafting efficiencies, defined as the percentage by weight of the total polystyrene added to a grafting reaction which was finally identified as grafted polystyrene in the product, were in good agreement with the calculated polymer function-

alities. For polymer E, the calculated functionality was an overestimate of the grafting capability of the polymer, as would be expected from the interference of the short wavelength absorption tail in the u.v. spectrum. The comparison is not meaningful for polymer F.

The preparation of the azodicarboxylate-functional polystyrenes followed a fairly lengthy chemical sequence (four steps from polystyryl carbanion, excluding protonation of the alkoxide ion). The average efficiency per reaction step for polymer C was 92% and for polymer A, 95%. As might be expected, the efficiency decreased at higher molecular weights where the effects of impurities in solvents would be more pronounced on a molar basis.

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