Graft copolymers from azodicarboxylate-functional pre-polymers: 2. Preparation in solution of graft copolymers of polydiene with polystyrene

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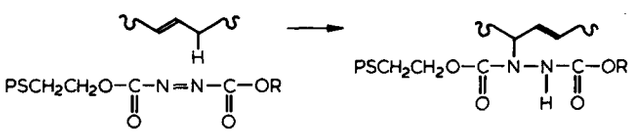
The preparation of graft copolymers of polyisoprene and polybutadiene with polystyrenes having molecular weights in the range 3800–17700 is described. Grafting is achieved by the cycloaddition of a terminal azodicarboxylate function on the polystyrene to the unsaturation of the polydiene. The kinetics of the reaction with polyisoprene at 60°C in toluene and cyclohexane solutions are presented. In the absence of impurity, the efficiency of the cycloaddition reaction is shown to be close to 100%. A simple fractionation procedure capable of reducing the amount of unbound polystyrene in the graft copolymer to very low levels is described.

(Keywords: polyisoprene; natural rubber; polybutadiene; polystyrene; azodicarboxylate; graft copolymer)

INTRODUCTION

The preparation of poly(isoprene-*g*-styrene) copolymers by reaction between polyisoprene and terminally-monofunctional polystyrene either in solution[1] or during dry mixing of the polymers[2] has been reported briefly. This paper details the preparation of poly(diene-*g*-styrene) copolymers in solution, characterization of the copolymers, and a suitable fractionation procedure for the removal of unbound polystyrene.

The function carried by the polystyrene is an azodicarboxylate moiety, which undergoes cycloaddition to the allylic double bond system of polydienes. The



reaction is well documented[3], and it has been used in the past to crosslink polydienes[4] and also to modify polydienes with low molecular weight groups[5,6]. One synthetic route to azodicarboxylate-functional polystyrene suitable for grafting to polydienes has been detailed recently[7].

The approach to the preparation of graft copolymers adopted here is novel in that both the backbone (polydiene) and graft (azodicarboxylate-functional polystyrene) polymers are stable under normal conditions. One advantage of the approach is the ability to fully characterize the backbone and graft molecules prior to the formation of the graft copolymer. It will be shown that the cycloaddition reaction is highly efficient in the absence of non-polymer impurities, so that grafting efficiencies are essentially governed by degree of azofuctionality of the polystyrene. It is therefore possible to readily prepare graft copolymers with desired compositional, molecular weight, and average graft frequency characteristics. The precise distribution of the graft sites is not identified at this point. A simple procedure for fractionating the unreactive polystyrene pre-polymer from the graft copolymer will be described.

EXPERIMENTAL

Materials

The synthesis and characterization of the azodicarboxylate-functional polystyrenes used here have been described in detail[7]. Molecular weights and functionalities are reproduced in *Table 1*.

The polydienes used were a lightly-masticated natural rubber (SMR 5L), a synthetic polyisoprene of pre-

Table 1 Characteristics of the azodicarboxylate-functional polystyrenes

Polymer	$\bar{M}_n$	*d*	Azo-functionality (%)
A	3200	1.07	76
B	5500	1.11	71
C	8200	1.06	68
D	8900	1.11	74
E	12700	1.04	68
F	17700	1.12	

$\bar{M}_n$ and dispersity index (*d*) determined by g.p.c. without correction for column broadening

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Table 2 Characteristics of the polydiene backbone polymers

Polymer	*cis*-1,4- (%)	*trans*-1,4- (%)	3,4 (%)	1,2 (%)	$\bar{M}_n \times 10^{-3}$	*d*
SMR 5L	100				540	4.0
Cariflex IR-305	92	4.5	3.5		690	2.2
Intene 55NF	35	53		11	125	2.2

Cariflex IR-305 is supplied by the Shell Chemical Co.
Intene 55NF is supplied by ISR
$\bar{M}_n$ by membrane osmometry, dispersity index (*d*) by g.p.c.

dominantly *cis*-1,4 configuration (Cariflex IR-305) and a polybutadiene with a high 1,4-content (Intene 55NF). Microstructures and molecular weights are given in *Table 2*.

Dry, olefin-free cyclohexane was obtained by the procedure described previously[7]. Analar grade toluene was used as received. Tetrahydrofuran was redistilled from lithium aluminium hydride under a nitrogen atmosphere prior to use.

Synthetic procedure

The preparation of graft copolymer was generally carried out on a 10 g scale in cyclohexane solution at 60°C, but some grafting reactions were also performed on a smaller scale in toluene and tetrahydrofuran solutions. Polydiene and polystyrene solutions were prepared separately and mixed to give compositions in the range 20–40 wt% polystyrene at a total polymer concentration of 2.86% w/v. The gas space was flushed with nitrogen and the sealed vessel was held at 60°C in a thermostatically controlled bath for 6 days.

An aliquot (10 ml) of the solution was evaporated to dryness under reduced pressure and the graft copolymer was dried *in vacuo* at 30°C to provide a sample for analysis. The bulk of the graft copolymer was isolated by the slow addition of 2 volumes of ethanol to the stirred solution. The precipitated graft copolymer was dried *in vacuo* at 30°C.

Graft copolymers were fractionated to remove unbound polystyrene by titrating 2.78% w/v solutions in toluene, containing 2% w/v Nonox WSP antioxidant, with ethanol to a cloud point at 60°C. Typically, the volume of ethanol required was 0.5–0.6 of the volume of the toluene solution. The cloud was redissolved at 65°C and the solution was allowed to cool slowly to *ca.* 25°C overnight. The clear, mobile, upper phase, which constituted the larger volume, was decanted from the cloudy, viscous lower layer. The latter was coagulated by the addition of ethanol and the graft copolymer was dried as before.

Polymer characterization

Infra-red spectra of graft copolymers were recorded on a Perkin-Elmer 157 spectrometer. Thin films were cast from the reaction solution directly onto NaCl plates, and spectra were recorded within ~15 min of sampling the reaction solution.

Gel permeation chromatograms of the graft copolymers were obtained in tetrahydrofuran solution (0.1% w/v) at a flow rate of 2 ml/min on five PL Gel columns (Polymer Laboratories; nominal pore sizes 10^6, 10^5, 10^4, 10^3 and 5×10^2 Å) using a Perkin-Elmer PE601 pump and LC55 ultra-violet detector operating at either 215 nm or 262 nm. At 262 nm, the reponse to polyisoprene is negligably small compared with the reponse to polystyrene. However, the polybutadiene gave a small but significant response at 262 nm and a suitable small correction was therefore applied to the area of the copolymer peak in the analysis of grafting efficiencies. A lower flow rate, 1 ml/min, was used in the estimation of the molecular weights of the polydienes and polystyrenes. The columns were calibrated with polystyrene or polyisoprene standards, as appropriate.

Membrane osmometry was performed on AR toluene solutions using a Mecrolab 501 osmometer.

The fractionated graft copolymers were anlysed for polystyrene content either by ^{1}H n.m.r. spectroscopy in $CDCl_3$ solution on a Perkin-Elmer R32 spectrometer or by derivative thermogravimetry (d.t.g.)[8] on a Stanton Redcroft TG-750 thermogravimetric analyser.

RESULTS AND DISCUSSION

The azodicarboxylate function exhibits a characteristic, strong absorption in the infra-red at *ca.* 1785 cm^{-1} due to the two carbonyl groups (*Figure 1*). After the cycloaddition reaction with the polydiene, the two carbonyl groups of the adduct which constitutes the graft site are no longer equivalent. The graft site is therefore characterized by two weaker absorptions in the infra-red at *ca.* 1770 and 1725 cm^{-1} (*Figure 1*). The grafting reaction may be conveniently followed by monitoring the changes in the carbonyl region of the infra-red spectra of polymer films cast from the reaction mixture. Completion of the reaction is best judged by the disappearance of the absorption at 1785 cm^{-1}, but the kinetics of the reaction are best determined by measurement of the absorption at 1725 cm^{-1}.

The kinetics of the grafting reaction between azodicarboxylate-functional polystyrene A and Cariflex IR-305 polyisoprene were studied in cyclohexane and toluene solution at 60°C. The concentration of the graft site was estimated from the absorbance at 1727 cm^{-1} relative to that at 1665 cm^{-1} due to the unsaturation in

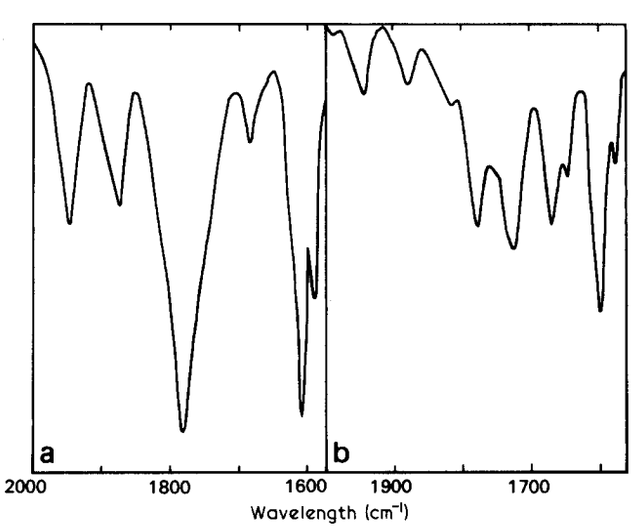

Figure 1 Infra-red spectra of azodicarboxylate-functional polystyrene A (a) and a graft copolymer of Cariflex IR-305 containing 40 wt% of the polystyrene (b)

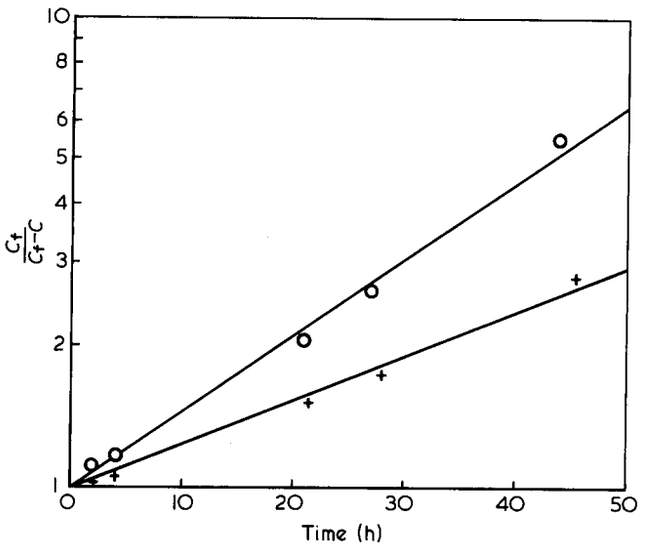

Figure 2 Log $(C_f/(C_f - C))$ as a function of reaction time for polystyrene A and Cariflex IR-305 in cyclohexane (○) and toluene (+) solutions at 60°C

the polyisoprene. The change in the concentration of double bonds of 1 mol% due to the formation of graft copolymer containing 40 wt% polystyrene was considered to be negligible.

Although the addition reaction is second order[3], the almost constant concentration of double bonds throughout the reaction leads to pseudo-first order kinetics. Thus, plots of $\log(C_f/(C_f - C))$ against t, where C_f and C are the concentration of the graft site at the end of the reaction and at time t, are linear (*Figure 2*). The pseudo-first order rate constants are 1.04×10^{-5} and 6.21×10^{-6} s^{-1} for the reaction in cyclohexane and toluene respectively. Given that the concentration of the isoprene repeat unit was 0.252 mol l^{-1}, the second order rate constants may be calculated to be 4.14×10^{-5} and 2.47×10^{-5} 1 mol^{-1} s^{-1} respectively.

The second order rate constants are of the order of those observed for the reaction of diethyl azodicarboxylate with 2-methylpent-2-ene in benzene solution[9]. Furthermore, the ratio of the two rate constants (1.68) is similar to that of the rate constants for the reaction of diethylazodicarboxylate with 2-methylpent-2-ene in methylcyclohexane and benzene at 100°C[9]. This suggests that the difference in rate of the grafting reaction in cyclohexane and toluene solutions is due to a solvent effect on the cycloaddition reaction rather than to a difference in the interaction of the two polymer reactants in the differing solvent media.

When tetrahydrofuran is used as the solvent for the grafting reaction, there is a rapid loss of azodicarboxylate function at 60°C accompanied by gelation of the polymer mixture. The infra-red spectrum of the dried gel provides no clear evidence of grafting. There are peaks at 1730, 1760 and 1780 cm^{-1}. It is probable that much of the azodicarboxylate function is consumed in a side-reaction with tetrahydrofuran. Tetrahydrofuran is prone to thermal addition to azodicarboxylates[10]. There is evidence that the addition reaction involves free-radicals, which would suggest that the observed gelation is due to free-radical crosslinking of the polyisoprene.

Graft copolymers were routinely prepared in cyclohexane solution at 60°C and with a reaction time of 6 days. It has been found that grafting reactions may be performed in toluene at 100°C with no reduction in grafting efficiency. Under these conditions, a reaction time of 48 h is adequate.

The efficiency of the grafting reaction may be assessed by gel permeation chromatography (g.p.c.) of the polymer recovered from the grafting reaction. The chromatogram comprises two peaks (*Figure 3*); a narrow peak at a retention time identical to that of the azodicarboxylate-functional polystyrene and a broader one at a shorter retention time. The former represents unbound polystyrene, the small shoulder being due to coupled polystyrene formed in the synthesis of the azodicarboxylate function[7]. The peaks at a high molecular weight may be attributed to the graft copolymer, because essentially identical retention times are observed for this peak when the u.v. detector is set to respond to polystyrene only (262 nm) or to both polystyrene and polyisoprene (215 nm). When the u.v. detector is operated at 262 nm, the grafting efficiency is given by the ratio of the area under the graft copolymer peak to the total area under both the copolymer and unbound polystyrene peaks.

The estimation of grafting efficiency is best performed on a sample of polymer recovered from the final reaction solution by evaporation to dryness. If the estimation is carried out using polymer which has been recovered by precipitation, it is necessary to first determine the total polystyrene content by some suitable technique, such as n.m.r. spectroscopy. The total polystyrene content will be less than the designed composition due to the failure of some of the unbound polystyrene to precipitate during the recovery of the polymer. The n.m.r. analysis introduces further experimental error into the estimation of the grafting efficiency.

Grafting efficiencies obtained in the preparation of graft copolymers from the synthetic polyisoprene Cariflex IR-305 and azodicarboxylate-functional polystyrenes with various $\bar{M}_n$ are presented in *Table 3*. The values are generally close to the analysed azodicarboxylate function-

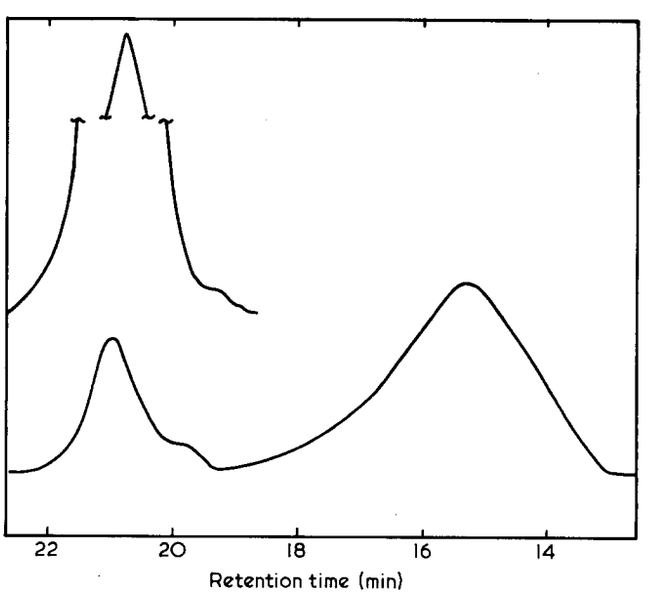

Figure 3 G.p.c. chromatograms of a graft copolymer of Cariflex IR-305 containing 20 wt% polystyrene and of the polystyrene pre-polymer, D, at equivalent polystyrene concentrations. U.v. detector operating at 262 nm

Table 3 Grafting efficiencies for graft copolymers of Cariflex IR-305

Polystyrene			Polystyrene in fractionated copolymer		
Polymer	Amount (wt%)	Grafting efficiency (%)	Calculated from *GE* (wt%)	Total observed (wt%)	Unbound (wt%)
C	20	71	15	15	0.09
C	25	71	19	19	0.11
C	30	73	24	24	0.17
C	35	73	28	29	0.29
C	40	72	33	33	0.39
A	40	77	34	33	–
B	40	73	33	29	–
D	40	77	34	33	0.41
E	40	59	28	33	–
F	40	67	31	33	–

Grafting efficiencies (*GE*) determined by g.p.c.

Table 4 Grafting efficiences for graft copolymers of natural rubber

Polystyrene			Polystyrene in fractionated copolymer	
Polymer	Amount (wt%)	Grafting efficiency (%)	Calculated from *GE* (wt%)	Total observed (wt%)
B	20	58	13	12
B	30	62	21	18
B	40	66	31	28
A	40	78	34	31
C	40	65	30	30
D	40	68	31	29
E	40	46	23	22
F	40	37	20	22

Grafting efficiencies (*GE*) determined by g.p.c.

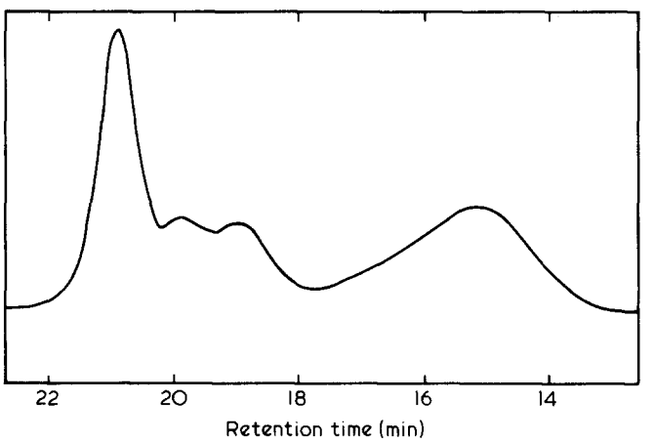

Figure 4 G.p.c. chromatogram of a graft copolymer of natural rubber containing 20 wt% polystyrene D. U.v. detector operating at 262 nm

alities of the polystyrenes (*Table 1*). There was no dependence of grafting efficiency on composition of the graft copolymer for any of the polystyrene pre-polymer, although for brevity results over a composition range are only presented for one polystyrene. These observations suggest that there is little or no side-reaction during the grafting process and that grafting efficiency is determined by the functionality which was achieved in the preparation of the polystyrene. Indeed, our experience suggests that reaction with Cariflex IR-305 followed by g.p.c. analysis for grafting efficiency is the most reliable and accurate method of accessing the functionality of azodicarboxylate-functional polymers. Polystyrenes A–D gave grafting efficiencies which are slightly higher than the analysed azodicarboxylate functionalities, probably because the value for the extinction coefficient of the azodicarboxylate function on polystyrene used in the spectroscopic analysis is uncertain to within a few percent[7]. The discrepancy between the grafting efficiency given by polystyrene E and the analysed azodicarboxylate functionality of the polymer is due to interference by a short wavelength absorption tail in the spectroscopic analysis of azodicarboxylate[7]. Spectroscopic analysis of polystyrene F was not possible, because the short wavelength absorption tail completely masked the expected weak azodicarboxylate peak.

The grafting efficiencies obtained in the preparation of graft copolymers of natural rubber (*Table 4*) are significantly lower than the analysed azodicarboxylate-functionalities of the polystyrenes, with the exception of that for the polystyrene of lowest $\bar{M}_n$. Furthermore, there are trends of decreasing grafting efficiency with decreasing polystyrene content of the copolymer and of increasing difference between the efficiency of grafting to Cariflex IR-305 and to natural rubber with increasing polystyrene $\bar{M}_n$. These trends can be ascribed to the reaction of azodicarboxylate function with some of the non-polyisoprene constituents of natural rubber. The ratio of impurity to azodicarboxylate function increases as the designed polystyrene content of the copolymer decreases and the $\bar{M}_n$ of the polystyrene increases. Some of the side-reaction leads to coupling of two or more polystyrene molecules, as evidenced by the presence of additional peaks in the g.p.c. chromatogram of a natural rubber graft copolymer (*Figure 4*).

Grafting efficiencies obtained in the preparation of graft copolymers of the polybutadiene Intene 55NF also generally fall below the values attained in the grafting of Cariflex IR-305 (*Table 5*). However, the former system exhibits a trend of decreasing grafting efficiency with increasing polystyrene content of the copolymer. The infra-red spectra of the copolymers show no evidence of side-reaction of the azodicarboxylate function, but reveal that the reaction of the azodicarboxylate was incomplete under the conditions used. The incomplete reaction of the azodicarboxylate is probably due to a lower rate for the

Table 5 Grafting efficiencies for graft copolymers of Intene 55NF

Polystyrene			Polystyrene in fractionated copolymer	
Polymer	Amount (wt%)	Grafting efficiency (%)	Calculated from *GE* (wt%)	Total observed (wt%)
B	20	68	15	15
B	30	67	22	23
B	40	63	30	33
F	20	59	13	16
F	30	57	20	21
F	40	54	27	27

Grafting efficiencies (*GE*) determined by g.p.c.

cycloaddition reaction with 1,2-disubstituted olefin than with trisubstituted olefin[3]. The decrease in grafting efficiency with increasing polystyrene content of the copolymer can then be explained by the decrease in polybutadiene concentration as the polystyrene content of the reaction solution is increased at a fixed total polymer concentration.

In the past, it has often proved difficult to separate efficiently graft copolymer from unbound graft chains and ungrafted backbone polymer. The majority of the graft copolymers reported here have a high degree of grafting, i.e. large number of grafts per backbone, which should ensure the complete absence of ungrafted backbone polymer. The large difference between the molecular weights of the polystyrene and polydiene facilitates the separation of unbound polystyrene from graft copolymer. A single cloud point titration of toluene solution with ethanol at an elevated temperature, followed by re-dissolution of the cloud at a slightly higher temperature and slow cooling, is sufficient to give graft copolymer almost free of unbound polystyrene. G.p.c. analysis of fractionated graft copolymers demonstrates that residual unbound polystyrene contents are typically less than 0.5% (*Table 3*). Although the procedure gives graft copolymer with a very low level of polymeric impurity, recovery of the graft copolymer is incomplete. A small proportion of the graft copolymer remains in solution with the unbound polystyrene. This is not a serious deficiency, because the unbound polystyrene is not required for characterization. The pre-polymer approach to the preparation of graft copolymers allows complete characterization of the graft species prior to the grafting reaction.

The composition of a fractionated graft copolymer may be compared with that calculated from the grafting efficiency determinated by g.p.c. Thus,

$$\text{Polystyrene content (wt\%)} = \frac{DC \times GE}{[100 - DC(1 - GE/100)]}$$

where DC is the designed polystyrene content in wt% and GE is the percentage grafting efficiency. The polystyrene contents of the fractionated graft copolymers were estimated either by ^{1}H n.m.r. spectroscopy or by derivative thermogravimetry. The techniques are of comparable accuracy, but the latter has the advantage of rapidity because it does not require dissolution of the polymer. The observed polystyrene contents are generally close to those calculated from the grafting efficiencies (*Tables 3*, *4* and *5*).

The procedures presented here allow the preparation of well-defined graft copolymers with very low levels of polymeric impurity. The ability to define the compositional and molecular characteristics of the graft copolymer arises from the pre-polymer approach; the extremely high efficiency of the cycloaddition reaction between azodicarboxylate-functional polystyrene and clean polydiene; and the ease of removal of unbound polystyrene from the graft copolymer. The procedures may be applied to other azodicarboxylate-functional polymers, as will be shown in further publications.

The graft copolymers are phase-separated and have properties broadly similar to those of styrene–diene–styrene block copolymers. A detailed presentation of the physical properties of the graft copolymers will be the subject of a future publication.

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REFERENCES

1 Campbell, D. S., Loeber, D. E. and Tinker, A. J. *Polymer* 1978, **19**, 1106
2 Campbell, D. S., Loeber, D. E. and Tinker, A. J. *Polymer* 1979, **20**, 393
3 Hoffmann, H. M. R. *Angew. Chem. Int. Edn.* 1969, **8**, 556
4 Flory, P. J., Rabjohn, R. and Shaffer, M. C. *J. Polym. Sci.* 1949, **4**, 225
5 Porter M. Plastics and Rubber: Materials and Applications, 1978, Feb., p 32
6 Siewak, J. W., Bryant, L. A. and Schulty, D. N. *J. Appl. Polym. Sci.* 1981, **26**, 4331
7 Campbell, D. S., Loeber, D. E. and Tinker, A. J. *Polymer* 1984, **25**, 1141
8 Wake, W. C., Loadman, M. J. R. and Tidd, B. K. 'Analysis of Rubber and Rubber-like Polymers', 3rd Edn., Applied Science, London, 1983, p 153
9 Knight, G. T. and Wildgoose, J. unpublished results
10 Ahlgren, G. *Tetrahedron Lett.* 1974, **33**, 2779