Poly(isoprene-g-alkyl methacrylate) copolymers: 2. Graft copolymer formation from azodicarboxylate functional methacrylate prepolymers

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Poly(isoprene-g-alkyl methacrylate) copolymers are prepared by reaction of the corresponding azodicarboxylate functional poly(alkyl methacrylates) with natural rubber (100% *cis*-1,4-), a commercial polyisoprene (92% *cis*-1,4-) and a purpose-synthesized polyisoprene (81% *cis*-1,4-polyisoprene) in toluene solution. Grafting efficiencies are determined and samples of graft copolymer are obtained free from methacrylate homopolymer by fractionation. Reaction also occurs in blends of polyisoprene and azodicarboxylate functional poly(alkyl methacrylate) with varying degrees of facility, depending on the difference in solubility parameters of the pairs of reacting polymers.

(Keywords: polyisoprene poly(n-butyl methacrylate); poly(n-hexyl methacrylate); poly(n-dodecyl methacrylate); poly(n-octadecyl methacrylate); end-groups; azodicarboxylate graft)

INTRODUCTION

We have reported the preparation of poly(isoprene-g-styrene) copolymers by cycloaddition of azodicarboxylate end groups on polystyrene chains to the allylic double bond system of the polyisoprene[1-3]. The cycloaddition reaction of the azodicarboxylate group is a well-defined process[4] which is not to be confused with the free radical initiation processes associated with azo-bis(2-methylpropionitrile) and related compounds. We now describe the use of this cycloaddition process in the preparation of graft copolymers of polyisoprenes with poly(butyl methacrylate) (PBMA), poly(hexyl methacrylate) (PHMA), poly(dodecyl methacrylate) (PLMA) and poly(octadecyl methacrylate) (PSMA). Preparation of the azodicarboxylate functional poly(alkyl methacrylates) has been described separately[5]. The present paper deals with the grafting reactions in toluene solution and fractionation of the initial products to give graft copolymer free from homo-poly(alkyl methacrylate). We also discuss criteria which will allow the grafting reaction to proceed in a blend of the appropriate polymer pairs in the absence of a common solvent.

EXPERIMENTAL

Instrumentation

Membrane osmometry (m.o.) was performed on a Hewlett-Packard 501 high-speed osmometer in toluene at 25°C using a Sartorius SM11539 membrane conditioned progressively in methanol/water, ethanol and toluene. ^{1}H nuclear magnetic resonance (n.m.r.) spectra were obtained at 90 MHz on a Perkin–Elmer R32 spectrometer at room temperature. The samples were analysed as solutions in deuterochloroform with hexamethyldisiloxane as an internal standard ($\delta = 0.05$). The resonances at 5 ppm (vinylic proton on polyisoprene) and 3.8 ppm (α-CH_2 of the alkyl ester group) were used to determine relative amounts of polyisoprene backbone and poly(alkyl methacrylate) side chain.

Gel permeation chromatography (g.p.c.) was on Laboratory Data Control equipment at 25°C in tetrahydrofuran, using a set of five Micrel columns of nominal pore sizes 10, 1×10^2, 1×10^3, 1×10^4 and 1×10^5 nm, and a u.v. detector. Molecular weight measurements of the polyisoprenes by g.p.c. analysis used the calibration data of Subramaniam[6].

Materials and procedures

Natural rubber (NR) was commercial SMR 5L masticated on a two-roll mill to reduce the average molecular mass. After mastication, the rubber was extracted with hot acetone in a Soxhlet extractor for 18 h and dried to constant weight in vacuo at 30°C. Commercial synthetic polyisoprene was Cariflex IR 305 (Shell Chemical Co.) and was used directly from the bale. A third polyisoprene (PI 117) was prepared by anionic polymerization in cyclohexane solution using established high vacuum and break-seal techniques. The cyclohexane (May and Baker, commercial grade) was flash-distilled, stirred over 20% oleum for 16 h to remove unsaturated material, stirred over bicarbonate slurry and dried over magnesium sulphate. It was then passed through basic alumina (2.5 l/150 g), dried over 3A molecular sieve and distilled from calcium hydride immediately before use. Polymerization glassware was purged with living polystyrene solution in vacuo and rinsed by solvent distillation before reaction components were introduced.

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The polymerization mixture was prepared from purified cyclohexane (1 l), isoprene (Aldrich Chemical Co., Gold label; 1.7 mol) and a solution of sec-butyl lithium in cyclohexane (Aldrich Chemical Co.; 1.05×10^{-3} mol). Polymerization was allowed to proceed overnight at room temperature and was terminated by the introduction of a solution of acetic acid (1.77×10^{-3} mol) in cyclohexane. The polymer was recovered by precipitation into industrial methylated spirits and was dried in vacuo at 35°C.

For preparation of graft copolymers in solution, the appropriate polyisoprene and azodicarboxylate functional poly(alkyl methacrylate) were dissolved in toluene to give a total polymer concentration of approximately 2.8% w/v. The solution was purged with a stream of nitrogen and was heated at 100°C for 40 h. An aliquot of the reaction mixture was evaporated to dryness to provide a sample of total polymer for determination of grafting efficiency by g.p.c. analysis. The bulk of the polymer was then fractionated by addition of ethanol to the solution at 60°C until a uniform permanent cloud developed, raising the temperature to 65°C to clear the cloud and allowing the solution to cool slowly (18 h) to room temperature. The lower viscous layer was collected, washed with ethanol and dried in vacuo at 35°C. In most cases, g.p.c. analysis of the fractionated material showed no free poly(alkyl methacrylate). In the few cases where small amounts of residual unbound methacrylate were detected, two precipitations of the polymer from toluene solution into methanol served to reduce the level to below the limits of detection by g.p.c.

Reaction of the azodicarboxylate functional poly(alkyl methacrylates) with polyisoprene in the absence of a diluent was investigated by dissolving the polymers separately in dichloromethane at room temperature, mixing the solutions rapidly and immediately removing the solvent under reduced pressure on a rotary evaporator. The dry samples were then stored at 23°C and pieces were analysed by g.p.c. at intervals.

Grafting efficiencies are expressed as the percentage, by weight, of the poly(alkyl methacrylate) which became bound to the polyisoprene backbone. They were determined from the g.p.c. chromatograms of the total reaction products by peak area measurement of the component (unbound poly(alkyl methacrylate)) eluted immediately after the main polymer. There was no wavelength at which poly(alkyl methacrylate) could be detected without interference from polyisoprene. It was therefore not possible to obtain the grafting efficiency by direct comparison of peak areas for bound and unbound methacrylate in the same chromatogram. Detector response factors were determined for each of the poly(alkyl methacrylates) in the hydroxyl functional form at 262 nm and were used to determine absolute levels of unbound methacrylate in each chromatogram. Resolution of the unbound methacrylate and graft copolymer peaks was always incomplete. The unbound methacrylate peak was arbitrarily defined by dropping a vertical line from the minimum between the two peaks to the baseline of the chromatogram.

Grafting efficiency measurements were not used to define the compositions of the purified graft copolymers. These compositions were determined by n.m.r. analysis.

RESULTS AND DISCUSSION

Table 1 summarizes information on the molecular characteristics of the polyisoprene backbones used in the present work and also reproduces information on the azodicarboxylate functional poly(alkyl methacrylates) which was reported previously[5]. The polyisoprenes were selected primarily to provide a range of backbone molecular weights but this was not readily achieved without an associated variation in the *cis*-1,4- content of the polymers.

Tables 2–5 present information on the products of all the grafting reactions which were carried out in toluene solution at 100°C. The efficiency of grafting is generally below the estimated azodicarboxylate content of each of the poly(alkyl methacrylates), and in some instances it is very much lower. This is in contrast to earlier experience with azodicarboxylate functional polystyrene[2,3], where good agreement was obtained between expected and measured grafting efficiencies if the polyisoprene was free from contamination with non-isoprenic material which could interfere with the cycloaddition reaction. The lower grafting efficiencies of the alkyl methacrylate polymers were anticipated from the presence of a thioether group formed as part of the preparation sequence of the azodicarboxylate functional poly(alkyl methacrylates)[5].

Table 1 Molecular characteristics for backbone polymers and azodicarboxylate functional poly(alkyl methacrylate) prepolymers used in the grafting reactions

Polymer	Microstructure	G.p.c. $M_n \times 10^{-3}$	G.p.c. d	Osmometry ($M_n \times 10^{-3}$)	Azo content[a] (%)
IR 305	92% *cis*-1,4-, 4.5% *trans*-1,4-, 3.5% 3,4- and 1,2-	524	1.77	674[b]	–
PI 117	83% *cis*-1,4-, 12% *trans*-1,4-, 5% 3,4- and 1,2	120	1.09	117[b]	–
NR	Essentially 100% *cis*-1,4-	180	2.57	270[b]	–
PBMA	–	8.0	1.58	8.1[c]	70
PHMA	–	7.2	1.50	7.2[c]	61
PLMA	–	9.5	1.89	8.0[c]	61
PSMA	–	5.7	1.60	5.6[c]	Not measured

[a] U.v. estimate of the percentage of poly(alkyl methacrylate) chains having an azodicarboxylate end group
[b] Membrane osmometry
[c] Vapour phase osmometry

Table 2 Graft copolymers of PBMA on polyisoprenes

Backbone	PBMA content (%)[a] Total product (*P*)	Pure graft (*G*)	*F*	Grafting efficiency, g.p.c. (%)[b]	Average no. of graft sites per chain
IR 305	47	24	35	54	27
	50	41	69	72	59
	63	45	49	47	69
PI 117	30	17	48	53	3
	63	41	42	49	10
	87	58	21	21	20
NR	30	15	42	46	6
	47	34	57	52	17
	63	43	45	56	26

[a] Percentage by weight of total polymer weight
[b] Percentage by weight of the poly(alkyl methacrylate) that is bound to the backbone

Table 3 Graft copolymers of PHMA on polyisoprenes

Backbone	PHMA content (%)[a] Total product (*P*)	Pure graft (*G*)	*F*	Grafting efficiency, g.p.c. (%)[b]	Average no. of graft sites per chain
IR 305	30	15	42	66	17
	47	28	43	62	36
	63	44	47	52	74
	87	66	29	59	182
PI 117	30	7	18	46	1
	63	36	34	55	9
	87	64	27	50	29
NR	30	12	32	40	5
	47	23	33	41	11
	63	37	35	44	22

[a] Percentage by weight of total polymer weight
[b] Percentage by weight of the poly(alkyl methacrylate) that is bound to the backbone

Grafting efficiencies with NR tend to be lower than with the other backbones, but the difference is less pronounced for the present sample of extracted NR than has previously been observed for the reaction of azodicarboxylate functional polystyrene with un-extracted NR. One group of preparations (PSMA on PI 117) and two other individual preparations gave anomalously low grafting efficiencies. No explanation for these specific anomalies is available.

The grafting efficiencies obtained from g.p.c. analysis refer specifically to the total polymer mixture from a reaction. Compositions of purified graft copolymers were determined separately and more precisely by n.m.r. spectroscopy. From these compositions, and molecular weight data for the constituent polymers, the graft copolymers are characterized in terms of the average number of grafts per backbone chain and the number average molecular weight between graft sites.

For the purified graft copolymers, a quantity, F, can be defined as

$$F = \frac{100 \times G \times (100 - P)}{P \times (100 - G)}$$

where P is the poly(alkyl methacrylate) content of the total reaction product and G is the poly(alkyl methacrylate) content of the purified graft copolymer, both expressed as percentages by weight. F is a measure of the grafting efficiency as viewed from the composition of the purified graft copolymer. For many separations, the ratio of F to the grafting efficiency measured by g.p.c. is near unity (*Tables 2–5*), indicating that the separation of the uncombined methacrylate prepolymer occurred with little or no accompanying fractionation of the graft copolymer by chemical composition. However, in several instances the ratio is much less than unity and these represent separations where graft copolymer of higher than average methacrylate content has been lost along with the ungrafted prepolymer. The fractionations were performed by attaining a cloud point at a fixed temperature. The composition of the solvent–precipitant mixture at the cloud point varied from one separation to another and it is therefore not possible to offer a systematic discussion of the behaviour of each sample.

The full range of graft copolymers in *Tables 2–5* was prepared using toluene as a diluent. However, in the course of evaluating suitable reaction conditions for the preparations some anomalous grafting efficiency results

Table 4 Graft copolymers of PLMA on polyisoprenes

Backbone	PLMA content (%)[a] Total product (*P*)	Pure graft (*G*)	*F*	Grafting efficiency, g.p.c. (%)[b]	Average no. of graft sites per chain
IR 305	30	18	52	50	16
	47	31	50	58	33
	63	44	47	54	57
	87	59	22	53	104
PI 117	63	17	12	46	3
	75	39	21	48	8
	87	52	16	50	14
NR	30	17	49	44	6
	47	23	33	35	9
	63	38	37	43	18

[a] Percentage by weight of total polymer weight
[b] Percentage by weight of the poly(alkyl methacrylate) that is bound to the backbone

Table 5 Graft copolymers of PSMA on polyisoprenes

Backbone	PSMA content (%)[a] Total product (*P*)	Pure graft (*G*)	*F*	Grafting efficiency, g.p.c. (%)[b]	Average no. of graft sites per chain
IR 305	30	15	42	45	21
	47	24	35	52	37
	63	38	37	41	72
	87	56	19	27	150
PI 117	30	12	32	25	3
	63	26	21	25	7
	87	60	22	35	31
NR	30	12	32	41	7
	47	24	35	44	15
	63	38	37	47	29

[a] Percentage by weight of total polymer weight
[b] Percentage by weight of the poly(alkyl methacrylate) that is bound to the backbone

were noted and were identified as arising from continuation of the grafting process in dried samples of total polymer in the time interval between sample isolation and g.p.c. analysis. We reported earlier[7] that the reaction of azodicarboxylate functional polystyrene with polyisoprene required both a reaction temperature in excess of the T_g of polystyrene and a high degree of mechanical mixing. The measured T_g values for the poly(alkyl methacrylates) in the present work were all below room temperature[5]. All the dried total polymer samples therefore fulfilled one of the criteria established for the polystyrene reactions, but we were observing appreciable reaction in the absence of mechanical mixing. The observations were placed on a more systematic basis by preparing dried mixtures of azodicarboxylate functional poly(alkyl methacrylate) and IR 305 polyisoprene from dichloromethane solutions with a minimum of time delay and analysing the mixtures by g.p.c. at intervals.

All the methacrylate polymers reacted to a much greater extent under these conditions than did polystyrene polymer and the PLMA eventually attained a grafting efficiency which was close to that obtained for reaction in solution. A more quantitative discussion of these results requires that allowance be made for differences in molar concentration of polymer chains and azodicarboxylate groups in the different polymer mixtures. A translation to molar concentrations of polymer chains is readily achieved using w/w composition and polymer densities. A density of 0.913 was used for IR 305 polyisoprene and the densities listed by Van Krevelen[8] were used for PBMA, PHMA and PLMA. The data of Greenberg and Alfrey[9] were used to assign a value of 0.98 for the density of the partially crystalline PSMA at room temperature. Reliable assignment of the azodicarboxylate end group contents of each of the poly(alkyl methacrylates) is more difficult because of the discrepancies between the spectroscopic estimates of *Table 1* and the observed grafting efficiencies of *Tables 2–5*. We have chosen to use the average of the observed grafting efficiencies for each of the polymers with IR 305 polyisoprene in solution as a measure of the total azodicarboxylate content, with the omission of the lowest result for PSMA. Using this information, the grafting efficiency results for each methacrylate can be converted to moles of azo group reacted at a given time. The inevitable time delay in the preparation and initial sampling of the polymer mixtures resulted in significant amounts of reaction at the nominal zero time in some instances. For this reason, the extent of reaction at 30 h was used as a measure of the reactivity of the polymers, rather than an evaluated rate constant. The extent of reaction was normalized to an initial azodicarboxylate concentration of 3.0×10^{-3} mol l^{-1}. The normalization assumes a kinetic order in azodicarboxylate group. This is not unreasonable in the light of the kinetic behaviour of simple azodicarboxylate compounds[4] and the normalization was only required to provide correction over the concentration range 2.1×10^{-3}–3.2×10^{-3} mol l^{-1}.

The reactivity of the polymers is shown in *Figure 1* as a function of the difference in solubility parameter (δ) between the polyisoprene and the poly(alkyl methacrylate). Solubility parameters were evaluated from the group molar attraction constants of Hoy, by the procedure documented by Krause[10]. The error bars are derived from a $\pm 10\%$ uncertainty in the grafting

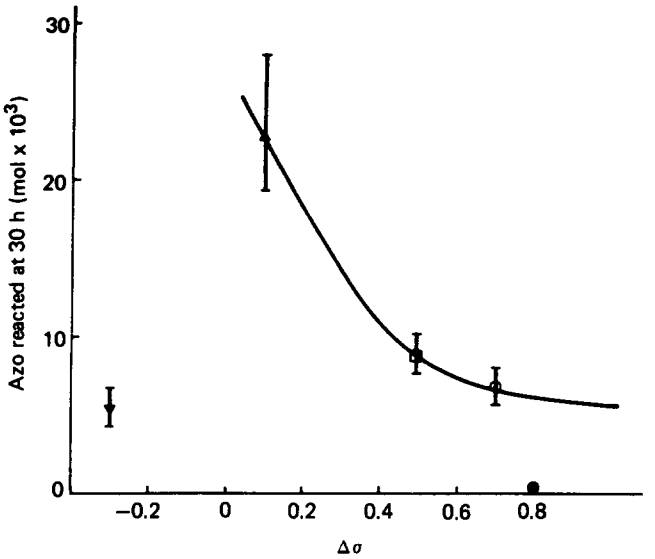

Figure 1 Reactivity of azodicarboxylate functional poly(alkyl methacrylates) and azodicarboxylate functional polystyrene with polyisoprene in the absence of diluent, as a function of the difference in solubility parameter between the polymer pairs: (○) PBMA; (□) PHMA; (△) PLMA; (▽) PSMA; (●) PS

efficiency figures used in the derivation. Through the series PBMA, PHMA, PLMA there is a consistent upward trend in the reactivity as the difference in the solubility parameter decreases, i.e. as the polyisoprene–poly(alkyl methacrylate) pairs approach potential miscibility on a molecular level. The reactivity of PSMA would be expected to lie between those of PHMA and PLMA on the basis of this trend, because the sign of the solubility parameter difference is not important in determining the potential miscibility of the polymers. The observed value is, in fact, the lowest of all the methacrylate polymers, although the probable uncertainties in the measurements made the reactivity indistinguishable from that of PBMA. We believe that the behaviour of PSMA in this context is a direct consequence of enhanced phase segregation caused by side chain crystallization of the octadecyl hydrocarbon chains of the ester alkyl groups. The crystallinity was observed in the azodicarboxylate functional polymer itself[4] and is also established by thermal and mechanical measurements on the graft copolymer. (These observations are part of more extensive work on the thermal and mechanical behaviour of the methacrylate graft copolymers which will be discussed in a subsequent publication.)

Comparison of the reactivities of PBMA and polystyrene (PS) show quite clearly that the T_g of the polymers in relation to the temperature of reaction is also important. The polystyrene sample was some 70°C below its T_g under the conditions of these experiments, whereas the PBMA was some 10°C above its T_g. Although the reactivity of the polystyrene was very low, it was not below the limits of detection. The implication is that the polystyrene was not totally locked into a hard phase incapable of interaction with the polyisoprene phase, but further discussion of this behaviour lies beyond the scope of the present measurements.

CONCLUSIONS

The 'ene' cycloaddition of azodicarboxylate end groups on a series of poly(alkyl methacrylates) has provided a

range of poly(isoprene-g-alkyl methacrylate)copolymers of varying poly(alkyl methacrylate) content. The reactions were less efficient than previously reported reactions of azodicarboxylate functional polystyrene but fractionation has provided samples of graft copolymer which are free from ungrafted poly(alkyl methacrylate).

Although reaction in toluene solution was used as the preparative method, extensive reaction in a static dry polymer mix was possible when polymer miscibility was favoured. Solubility parameter difference, glassy phase separation and polymer crystallization can all contribute to retardation of this dry mix reaction.

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