Poly(isoprene-g-alkyl methacrylate) copolymers: 1. Poly(alkyl methacrylates) with azodicarboxylate end groups

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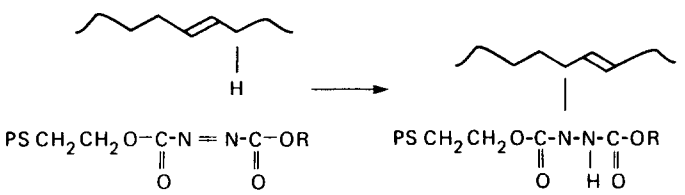
Synthesis of four poly(alkyl methacrylates) having different ester alkyl chain lengths (butyl-, hexyl-, dodecyl- and octadecyl-) and azodicarboxylate end groups is described. The molecular weights of the polymers are in the range 5×10^3–1×10^4, and between 60 and 70% of the polymer chains have azodicarboxylate functionality. Radical transfer constants for the alkyl methacrylates with 2-mercaptoethanol in benzene solution at 60°C are reported together with Mark–Houwink K and α constants required for gel permeation chromatography calibration.

(Keywords: poly(n-butyl methacrylate); poly(n-hexyl methacrylate); poly(n-dodecyl methacrylate); poly(n-octadecyl methacrylate); 2-mercaptoethanol; transfer end-groups; azodicarboxylate)

INTRODUCTION

The azodicarboxylate functional group reacts with allylic unsaturation by cycloaddition[1]. We have shown that polystyrene chains having the azodicarboxylate function as an end group can be grafted on to polydiene chains by means of this cycloaddition process[2–4] (Scheme 1) and



Scheme 1

that the products behave as thermoplastic rubbers within a suitable range of composition. The grafting process potentially offers a degree of control over the graft copolymer structure which is not commonly available and we have had some interest in exploring its range of application. This report describes the preparation of a series of four poly(alkyl methacrylates) having terminal azodicarboxylate functional groups and their characterization in terms of molecular weight and end group content. The grafting reactions and the properties of the grafted products will be the subject of future publications.

Preparation of polymers with azodicarboxylate end groups requires, in the first instance, preparation of the corresponding hydroxyl functional polymers. This is readily achieved with polystyrene by anionic polymerization followed by reaction of the polymeric carbanion with ethylene oxide[5]. The corresponding reactions with methacrylate monomers are less reliable. In particular, the lower nucleophilic reactivity of the poly(alkyl methacrylate) carbanion causes difficulties. McGrath *et al.*[6] have shown that many of the problems associated with anionic polymerization of methacrylates can be overcome by proper purification of the monomer and Anderson *et al.*[7] have successfully prepared hydroxyl functional poly(methyl methacrylate) by anionic polymerization using a protected hydroxyl function on a highly hindered initiator. More recently, hydroxyl functional poly(methyl methacrylate) has been prepared by the novel 'group transfer' polymerization procedure of Webster *et al.*[8,9] However, the present programme of work was under way before these developments in methacrylate polymerization chemistry were generally known. Our polymers were prepared by free radical polymerization in the presence of 2-mercaptoethanol as chain transfer reagent[10,11].

The polymers of interest in our programme were those derived from butyl-, hexyl-, dodecyl- (lauryl) and octadecyl- (stearyl) methacrylates. They will be referred to as PBMA, PHMA, PLMA and PSMA respectively. Molecular weights in the region of 5×10^3–1×10^4 were appropriate for our interest in physical properties of the graft products. Neither Mark–Houwink constants (for molecular weight calibration by gel permeation chromatography (g.p.c.)) or radical chain transfer constants were available in the literature for all four systems. Our experimental values are reported here.

EXPERIMENTAL

Instrumentation

U.v. and visible spectra were recorded on a Pye Unicam SP8-100 spectrometer. Vapour pressure osmometry (v.p.o.) was performed on a Corona Wescan 232A molecular weight apparatus at 50°C, using toluene as solvent and benzil as calibration standard. Membrane osmometry was performed on a Hewlett Packard 501 high speed membrane osmometer at 25°C using toluene as solvent. Intrinsic viscosities were

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measured in tetrahydrofuran at 25°C using classical Ubbelholde viscometers. G.p.c. used Laboratory Data Control equipment. Five Micrel columns of nominal pore sizes 10, 1×10^2, 1×10^3, 1×10^4 and 1×10^5 nm were run in series with an ultra-violet detector. The chromatograms were run at 25°C with tetrahydrofuran as solvent. A universal calibration procedure[12] was used to enable molecular weights of the poly(alkyl methacrylate) samples to be derived from a polystyrene calibration. For this purpose, established relationships[13] were used to calculate values of the Mark–Houwink constants in tetrahydrofuran from intrinsic viscosity and membrane osmometry measurements on the corresponding high molecular weight polymers and g.p.c. chromatograms run in conjunction with a broad distribution polystyrene standard.

Materials

Benzene and toluene (BDH, Analar grades) were dried by azeotropic distillation and redistilled. Dichloromethane (BDH, reagent grade) was redistilled from powdered calcium hydride immediately before use. Pyridene (BDH, reagent grade) was redistilled and stored over potassium hydroxide. 2-Mercaptoethanol and 2,2′-azo-bis(2-methylpropionitrile) (BDH, reagent grades) were used as supplied. n-Butyl and n-hexyl methacrylates (BDH, commercial grades) were shaken with an equal volume of aqueous sodium hydroxide (1 M) to remove stabilizers, washed repeatedly with distilled water and dried over calcium chloride. They were then dried over calcium hydride and redistilled under reduced nitrogen pressure (b.p.: BMA, 47–50°C, 8 Torr; HMA 130–140°C, 2 Torr). Lauryl and stearyl methacrylates (Pfaltz and Bauer Inc.) were each dissolved in an equal volume of redistilled benzene and washed with sodium hydroxide solution. The organic layer was washed repeatedly with distilled water and dried by azeotropic distillation. Finally, 25% by volume of the benzene was distilled from the monomer solution and replaced with dry benzene to give monomer concentrations of 57.8 and 72.2% for LMA and SMA respectively. All purified monomers were stored under nirogen at −25°C.

Polymerization of alkyl methacrylates

Polymerization of the alkyl methacrylates was carried out in a 1 l three-neck flask equipped with Sovirel screw fittings and a mechanical stirrer. The dry apparatus was assembled and flushed with nitrogen. Benzene, AIBN, 2-mercaptoethanol and alkyl methacrylate monomer were added and the pressure in the flask was reduced until the benzene started to boil. The vacuum was immediately broken with nitrogen. The procedure was repeated and the flask was closed under a small positive pressure of nitrogen and immersed in a thermostatted bath at 60°C. The reaction time was 20 h for SMA and 16 h for the other methacrylates. An aliquot of each reaction solution was taken after the reaction period and evaporated to dryness to provide total polymer for transfer constant evaluation. Main fractions of hydroxyl-tipped PBMA and PHMA were isolated by precipitation into a 10-fold excess of methanol and the hydroxyl-tipped PSMA into ethanol. The hydroxyl-tipped PLMA was isolated by removal of the solvent by evaporation under reduced pressure and washing the residual viscous liquid repeatedly with methanol before drying. The different isolation procedures were dictated by the properties of the individual products. Non-functional poly(alkyl methacrylates) were prepared using the same reaction conditions but in the absence of 2-mercaptoethanol.

End group synthesis and characterization

Reagents for the conversion of hydroxyl functional polymer to azodicarboxylate functional polymer will be discussed in more detail elsewhere. In the present work both 2-carbethoxyazocarbonyl chloride (CEAC) and 5-chlorocarbonylpentyl ethyl azodicarboxylate (CPEA) were used. Polymer samples (10 g, approx. 1.25×10^{-3} moles, depending on the molecular weight) were freed from low molecular weight hydroxylic material by azeotropic distillation in toluene and were evaporated to dryness. The polymer was then dissolved in dry dichloromethane (80 ml). Pyridiene (0.40 ml, 5.0×10^{-3} mole) was added, followed by CEAC or CPEA (5.0×10^{-3} mole) as a freshly prepared solution in dry dichloromethane and allowed to react at room temperature. Reaction time at room temperature was 3 h for CEAC and 4 days for CPEA. The polymers were recovered by adding a 10-fold excess of methanol to the reaction mixture and were dried *in vacuo* at 30°C.

The concentration of the azodicarboxylate groups in the modified polymers was measured using the characteristic absorption close to 410 nm. Spectra were recorded for 10% w/v solutions in dichloromethane. The solutions were not subject to the enhanced absorption previously reported for solutions of azodicarboxylate-terminated polystyrene[2]. An extinction coefficient of 34 was used to evaluate azodicarboxylate concentration.

RESULTS AND DISCUSSION

O'Brian and Gornick[14] give a value of 0.65 for the free radical chain transfer constant of 2-mercaptoethanol with methyl methacrylate in benzene at 60°C. Grezlak and Wilkes[11] report a value of 0.52. No values of the constants for the alkyl methacrylates of the present study were found in the literature. Preliminary experiments with butyl and lauryl methacrylates indicated that the transfer constants were close to unity, and the main preparations were performed on the assumption that a value of unity was appropriate for all the monomers. Experimental values for the transfer constants were, in due course, obtained using the molecular weight information on the samples of each polymer prepared for the evaluation of Mark–Houwink constants and the molecular weights of the hydroxyl polymers obtained either from the resultant g.p.c. calibration or from v.p.o. measurements. Only the transfer constant for PSMA differs appreciably from unity (*Table 1*), the deviation indicating an increased preference for hydrogen abstraction from the transfer agent relative to propagation of the polymer radical.

Mark–Houwink constants have been reported for tetrahydrofuran (THF) solutions of PMMA[15–19], PLMA[13] and PSMA[20–22]. The constant α shows little consistent trend with change of ester alkyl group and a mean value of 0.69 is representative. The values of K show some downward trend from about 1.2×10^{-2} to 0.6×10^{-2} dm^3 g^{-1} with increasing chain length but the trend is ill defined in relation to the scatter of the values. The α values obtained for the set of polymers in the

Table 1 G.p.c. calibration data for four poly(alkyl methacrylates) and transfer constants for polymerization in the presence of 2-mercaptoethanol

Polymer	$R \times 10^2$	$[\zeta]$ (dl g^{-1})	$M_n \times 10^{-5}$ (m.o.)	$K \times 10^{-4}$ (dl g^{-1})	α	G.p.c.[b] $M_n \times 10^{-5}$	G.p.c.[b] M_w/M_n	Transfer constant
PBMA	0	2.05	2.23	2.03	0.70	2.30	2.70	–
	2.09					0.058	1.82	1.13
PHMA	0	1.60	1.99	1.31	0.70	1.93	4.49	–
	2.79					0.054	1.87	1.09
PLMA	0	1.18[c]	2.47[c]	2.32	0.64	2.63	2.69	–
	2.45					0.094	1.90	1.04
PSMA	0	2.33	3.04	3.24	0.64	3.43	5.32	–
	5.60					0.039	2.05	1.52

[a] Initial molar ratio of transfer agent to monomer
[b] G.p.c. results after application of the calibration procedure
[c] Fractionated material was used for the K and α determination. The whole polymer had a low molecular weight tail, which caused membrane permeation. Subsequent g.p.c. determination of M_n for the whole polymer gave a value of 1.81×10^5 and this value was used in evaluating the transfer constant

present work (*Table 1*) are in reasonable agreement with the published values. The K values are slightly higher than expected.

The physical forms of the hydroxyl functional polymers are similar to those of the corresponding materials prepared in the absence of transfer reagent. For PBMA, PHMA and PLMA there is the expected trend from a hard polymer to a viscous liquid as the T_g decreases. The trend is reversed with PSMA, where crystallization of the hydrocarbon side chains results in a waxy solid[22]. The crystallinity was readily observed by optical microscopy, and a melting point of 35°C was recorded using a hot stage microscope. The value is in good agreement with published values of 33.5°C[23] and 37.5°C[24]. The molecular weight distributions of the whole polymer samples of the hydroxyl functional polymers were appreciably narrower than those of the polymers prepared in the absence of transfer agent (*Table 1*). For PBMA, PHMA and PSMA these distributions were reduced even further during purification of the main batches of polymer by re-precipitation (*Table 2*). A certain amount of fractionation was to be expected during reprecipitation when dealing with these relatively low molecular weight materials. The physical form of the PLMA discouraged conventional re-precipitation, and washing the gum with alcohol gave very little change in the molecular weight distribution. The hydroxyl functionality of the polymers was not specifically measured. From the chain transfer stoichiometry set out by Grezlak and Wilkes[11] and the molecular weight information in *Table 1*, the calculated hydroxyl functionalities were 95% or greater for all four polymers. However, these calculations apply strictly to the whole polymer and imply a uniform distribution of hydroxyl groups over the whole range of molecular weight. If there is any tendency for hydroxyl functionality to be concentrated towards the lower molecular weight end of the distribution, the fractionation during purification of the main batches of polymer may have slightly reduced the final hydroxyl functionality.

The hydroxyl functional methacrylate polymers contain a monosulphide group β- to the hydroxyl group[11]. This monosulphide is retained after acylation of the hydroxyl group to generate the azodicarboxylate functional polymers. Azodicarboxylates are known to react with monosulphides having a free α- hydrogen atom to give, initially, addition across the $>N=N<$ double bond[25]. The possible occurrence of this reaction in our azodicarboxylate functional polymers was clearly a source of some concern. The situation was potentially aggravated by the fact that the product of acylation of the hydroxyl polymer with the reagent 2-ethoxycarbonyl-azocarbonyl chloride seemed to offer possibilities for specific intramolecular reaction between the azo group and the monosulphide. The latter consideration prompted investigation of the alternative reagent, 5-chlorocarbonylpentyl ethyl azodicarboxylate, in which an alkyl chain was interposed between the azodicarboxylate and acid chloride groups, thus increasing the intramolecular separation between the azodicarboxylate and monosulphide groups in the functional polymer.

Table 2 Characterization of azodicarboxylate functional poly(alkyl methacrylates)

Polymer	Physical form	T_g[a] (°C)	$M_n \times 10^3$ G.p.c.	$M_n \times 10^3$ V.p.o.	M_w/M_n (g.p.c.)	Azo content[b] (%)
PBMA	Brittle solid	10	8.0	8.1	1.58	70
PHMA	Gum	−25	7.2	7.2	1.50	61
PLMA	Viscous liquid	−45	9.3	8.0	1.89	61
PSMA	Wax	[c]	5.7	3.6	1.60	–

[a] Measured on hydroxyl functional polymers
[b] 100 × (number of azo groups)/(total number of molecules)
[c] No transition seen down to −140°C

Samples of azodicarboxylate functional PBMA were prepared using each of the acylating agents and were heated in nitrogen-purged toluene at 100°C, both as 10% and as 1% w/v solutions. The characteristic azodicarboxylate absorption maximum close to 410 nm was observed with the intention of determining the rates of loss of the azodicarboxylate function. In the event, new absorption maxima developed close to the azodicarboxylate maximum and vitiated attempts at quantitative measurement. Qualitative observation of the spectra showed that loss of azodicarboxylate group did occur over a period of days, with some indication that the group with the extended alkyl chain decomposed less readily. However, the rates of decomposition were not fast in relation to the expected rates of grafting to polydienes in solution (40 h at 100°C for complete reaction) and there

were no strong grounds for preferring one acylating agent over the other. The extended chain reagent was used for preparation of the PBMA, PHMA and PSMA polymers and 2-ethyoxycarbonylazocarbonyl chloride was used for PLMA.

Estimates of the numbers of azodicarboxylate end groups were obtained using the u.v. absorption maximum at 410 nm, for PBMA, PHMA and PLMA (*Table 2*). The values are expressed as the percentage of polymer chains which carry azodicarboxylate functionality and are derived from the g.p.c. value for M_n and the apparent M_n derived from the u.v. absorption maximum. The numbers of azodicarboxylate groups are somewhat less than expected from the theoretical numbers of hydroxyl groups on the polymers. Subjecting samples of hydroxyl functional polymer to two consecutive acylation treatments failed to give a significant increase in the numbers of azodicarboxylate end groups between the first and second treatments, and could in fact result in some decrease in azodicarboxylate content. The standard acylating conditions were therefore accepted as being adequate to ensure complete reaction of the hydroxyl groups, and the less than ideal levels of azodicarboxylate groups are to be regarded as an indication of some loss of azodicarboxylate activity during recovery of the polymers from the acylation reaction mixture. An estimate of the azodicarboxylate content of the PSMA polymer was not obtained because of relatively high background absorption through the 410 nm region. The presence of functional group was, however, qualitatively confirmed.

All four azodicarboxylate functional polymers formed graft copolymers with polyisoprene when the polymers were allowed to react in solution. Certain aspects of the grafting process are of sufficient interest to warrant discussion at some length and for this reason the grafting reactions will be described in a separate paper.

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REFERENCES

1 Hoffmann, H. M. R. *Ang. Chem., Int. Edn.* 1969, **8**, 556
2 Campbell, D. S., Loeber, D. E. and Tinker, A. J. *Polymer* 1984, **25**, 1141
3 Campbell, D. S., Loeber, D. E. and Tinker, A. J. *Polymer* 1984, **25**, 1146
4 Campbell, D. S., Mente, P. G. and Tinker, A. J. *Kaut. Gummi* 1981, **34**, 636
5 Richards, D. H. and Szwarc, M. *Trans. Faraday Soc.* 1959, **55**, 1644
6 Allen, R. D., Smith, S. D., Loog, T. E. and McGrath, J. E. *ACS Polymer Prepr.* 1985, **26**, 247
7 Anderson, B. C., Andrews, G. D., Arthur, P. Jr, Jacobson, H. W., Melby, L. R., Playtis, A. J. and Sharkey, W. H. *Macromolecules* 1981, **14**, 1601
8 Webster, O. W., Herter, W. R., Sogah, D. Y., Farnham, W. B. and RajanBabu, T. V. *J. Am. Chem. Soc.* 1983, **105**, 5706
9 Sogah, D. Y., Herter, W. R. and Webster, O. W. *ACS Polymer Prepr.* 1984, **25**, 3
10 Gardlund, Z. G and Bator, M. A. K. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 1251
11 Grezlak, J. H. and Wilkes, G. L. *J. Appl. Polym. Sci.* 1975, **19**, 769
12 Coll, H. and Gilding, D. K. *J. Polym. Sci. A*-2 1970, **8**, 89
13 Mahabadi, H. K. and O'Driscoll, K. F. *J. Appl. Polym. Sci.* 1977, **21**, 1293
14 O'Brien, J. L. and Gornick, F. *J. Am. Chem. Soc.* 1955, **77**, 4757
15 Dobbin, C. J. B., Rudin, A. and Tchir, M. F. *J. Appl. Polym. Sci.* 1982, **27**, 1081
16 Rudin, A. and Hoegy, H. L. W. *J. Polym. Sci. A*-2, 1972, **10**, 217
17 Provder, T. and Rosen, E. M. *Sep. Sci.* 1970, **5**, 437
18 Chee, K. K. *J. Appl. Polym. Sci.* 1985, **30**, 1323
19 Hahabadi, H. K. L. *J. Appl. Polym. Sci.* 1985, **30**, 1535
20 Zhongde, Xu, Mingshi, S., Hadjichristidis, N. and Fetters, L. *Macromolecules* 1981, **14**, 1591
21 Fee, J. G., Port, W. J. and Witnaur, L. P. *J. Polym. Sci.* 1958, **33**, 95
22 Lal, J. and Trick, G. S. *J. Polym. Sci. A*-2 1964, **2**, 4559
23 Greenbers, S. A. and Alfrey, T. *J. Am. Chem. Soc.* 1954, **76**, 6280
24 Rogers, S. S. and Mandelkern, L. *J. Phys. Chem.* 1957, **61**, 985
25 Wilson, G. E. and Martin, J. H. *J. Org. Chem.* 1972, **37**, 2510