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Preparation and modification of itaconic anhydride–methyl methacrylate copolymers

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Abstract: The free radical copolymerisation of itaconic anhydride and methyl methacrylate in solution was studied at 60 °C. The copolymer composition was determined by ^{1}H-NMR spectroscopy and the obtained monomer reactivity ratios were calculated, $r_{ITA} = 1.35\pm0.11$; $r_{MMA} = 0.22\pm0.22$ (by the Fineman–Ross method) and $r_{ITA} = 1.27\pm0.38$; $r_{MMA} = 0.10\pm0.05$ (by the Mayo–Lewis method). The synthesised copolymers were modified by reaction with di-*n*-butyl amine. The copolymer composition after amidation was determined by elemental analysis *via* the nitrogen content. Amidation of the anhydride units in the copolymers with di-*n*-butyl amine resulted in complete conversion to itaconamic acid.

Keywords: copolymerisation, itaconic anhydride, methyl methacrylate, amidation, itaconamic acid.

INTRODUCTION

Copolymers containing both hydrophilic and hydrophobic segments (amphiphilic polymers) are drawing considerable attention because of their possible use in biological systems. *N*-Substituted itaconamic acids are strongly amphiphilic molecules. Homopolymers and copolymers obtained from such monomers may have wide applications. Various copolymer compositions can produce a very large number of different arrangements, producing materials of varying chemical and physical properties. Thus, the hydrophilicity of copolymers can be modified by changing the amount of incorporated itaconamic acid. Also, the alkyl side chain in these polymers can be varied, resulting in polymers with different side chain length, thus controlling the hydrophobicity.[1,2] However, poly(*N*-substituted itaconamic acid)s are difficult to obtain by direct polymerisation of their monomers and the preparation of itaconamic acids, by reaction of itaconic anhydride

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with amines, can be complicated.[3–5] Thus, the isomerisation of itaconic anhydride to citraconic anhydride occurs in the presence of amine. The rate of isomerisation depends on the amine base strength and solvent medium, with strong bases in a polar solvent resulting in a much faster isomerisation than weak bases in a non-polar solvent.[4] Also, the isolation and purification of the produced itaconamic acids can be difficult, particularly if they do not crystallise.[5]

Another convenient way of obtaining amphiphilic polymers is to functionalise polymers and copolymers. The modification of poly(itaconic anhydride) or its copolymers by different reactions (alcoholysis, hydrolysis, amidation) seems not to have been investigated extensively.[6–8] In the experiments presented in this paper, copolymers of itaconic anhydride and methyl methacrylate were modified by amidation with di-*n*-butyl amine. Hitherto, there have been no data reported on the amidation of such copolymers.

EXPERIMENTAL

Materials

Commercially available reagent grade chemicals were used for all the experimental work. Itaconic acid was supplied by Aldrich and used as received. Acetyl chloride and di-*n*-butyl amine (both obtained from Aldrich) were purified by distillation.

α,α'-Azobisisobutyronitrile (AIBN) was supplied by Aldrich and recrystallised from methanol.

Solvents used for the isolation, purification, reprecipitation and modification of the copolymers were dried over molecular sieves in order to minimise the hydrolysis of itaconic anhydride units in the copolymers.

Monomer and polymer preparation

Itaconic anhydride (ITA) was prepared by dehydrating itaconic acid with acetyl chloride following an improved previously reported procedure.[9] The crude itaconic anhydride was purified by several recrystallisations from chloroform. Anhydrous conditions were observed to minimise the hydrolysis of the anhydride to acid. White crystals with a melting point of 68−70 °C were obtained and the structure confirmed by ^{1}H-NMR and IR spectroscopy.

Methyl methacrylate (MMA) was washed with 10 % NaOH aqueous solution to remove inhibitor, washed with water to neutral, dried over calcium hydride and vacuum distilled.

Copolymers of itaconic anhydride and methyl methacrylate were prepared by the solution copolymerisation technique using AIBN as the initiator. A 100 ml three-necked flask equipped with a magnetic stirrer and condenser protected from moisture was used for the copolymerisations. The solution copolymerisations were performed under a nitrogen atmosphere using 2-butanone as the solvent. The desired amounts of itaconic anhydride and methyl methacrylate were dissolved in 2-butanone together with AIBN (0.25 mol %) in a three-necked flask. Nitrogen was bubbled for 15 minutes at room temperature through the solution before starting the polymerisation, while during the polymerisation the nitrogen stream was directed over the top of the condenser. A preheated water bath was employed to commence the polymerisations. The copolymerisations were performed at 60 °C for different times, depending on the composition of the monomer feed (Table I). The copolymers were precipitated in a ten-fold amount of methanol, redissolved in 2-butanone and reprecipitated twice in anhydrous diethyl ether. The copolymers were dried under vacuum at room temperature to remove the residual volatiles.

Amidation of the copolymers

A 50 ml three-necked flask, equipped with a magnetic stirrer, dropping funnel and condenser, protected from moisture, was used for the amidation reaction. A solution of freshly distilled di-*n*-butyl amine (1 g) in chloroform (10 ml) was added dropwise over 90 minutes to a well-stirred solution of a copolymer (0.2 g) in chloroform (15 ml) at 0 °C. The di-*n*-butyl amine was always in large excess to insure that the amidation went to completion. The reaction mixture was vigorously stirred for one day at room temperature. Only the copolymer from the feed composition of 2 mol % itaconic anhydride dissolved immediately in chloroform. The solubility of the copolymers in chloroform decreased with increasing amount of itaconic anhydride in the monomer feed. As the amidation reaction progressed, the copolymers dissolved, finally resulting in a colourless solution. The modified copolymers were precipitated in diethyl ether, dissolved in chloroform, reprecipitated into petroleum ether, and dried under vacuum to constant mass. White powdery polymers were obtained.

TABLE I. Preparation of ITA–MMA copolymers

Monomer feed, mol % ITA	Polymerisation time, min	Yield, wt %
2	45	3.14
6	50	2.48
11	60	1.85
20	105	1.62
30	240	2.27
40	360	6.41

Copolymer characterisation

The copolymers were characterised by ^{1}H-NMR spectrometry on a Varian GEMINI 200 instrument (200 MHz) using TMS as the internal standard and deuterochloroform and deuteroacetone as solvents for the modified and unmodified copolymers, respectively. Infrared spectra were obtained using a BOMEM, MB-Series FTIR spectrometer. The samples were recorded in KBr pellets. Elemental analysis measurements were performed using a Vario III CHNOS Elemental Analyzer, Elemental Analysen Systeme GmbH, to determine the nitrogen content in the copolymers.

The molar masses of the amidated copolymer samples were measured by gel permeation chromatography, GPC, at 30 ºC using a Waters 1500 Series instrument fitted with four analytical columns and an RI detector. Chloroform was used as the mobile phase at a flow rate of 1 ml min^{-1}. The columns were calibrated with narrow molar mass poly(methyl methacrylate) standards and the chromatograms were processed with Waters Breeze software. The molar masses of the unamidated copolymers and homopoly(itaconic anhydride) could not be measured by GPC due to lack of solubility in chloroform.

RESULTS AND DISCUSSION

Copolymers of itaconic anhydride and methyl methacrylate were obtained by free radical copolymerisation in 2-butanone using AIBN as initiator. The copolymer composition was determined by ^{1}H-NMR spectroscopy. The ratio of the signals at 3.65 ppm (associated with the hydrogen from the methylene group in the anhydride ring) and 3.57 ppm (associated with the hydrogen from the methyl ester group from methyl methacrylate) gave the copolymer composition. As these two peaks overlapped, they were deconvoluted using the PeakFit V.4 computer program. The determined copolymer compositions are given in Table II, from which it can be seen that the content if anhydride moieties was enriched in the copolymers with regard to the feed composition.

The monomer reactivity ratios for the copolymerisation of itaconic anhydride and methyl methacrylate determined by the Fineman and Ross method[10] are $r_{ITA} = 1.35 \pm 0.11$ and $r_{MMA} = 0.22 \pm 0.22$ and those calculated by the Mayo–Lewis method[11] are $r_{ITA} = 1.27 \pm 0.38$ and $r_{MMA} = 0.10 \pm 0.05$.

The free radical copolymerisation of itaconic anhydride–methyl methacrylate was previously reported by Cowie and co-workers,[12] who prepared copolymers by bulk copolymerisation at 70 °C. The values of the monomer reactivity ratios reported in this investigation, calculated by the Mayo–Lewis method, were $r_{ITA} = 0.99 \pm 0.40$ and $r_{MMA} = 0.18 \pm 0.07$. The monomer reactivity ratios for this system suggested that the copolymers were essentially statistical with little tendency towards alternation or the formation of long sequences of either type of monomer.

TABLE II. Composition of the prepared copolymers of methyl methacrylate and itaconic anhydride

mol % ITA in the monomer feed	mol % ITA in the copoymer
2	12.86
6	23.59
11	42.47
20	47.29
30	59.86
40	66.47

A comparison of the results of Cowie and co-workers with the data obtained in this study is shown in Fig. 1, from which it can be seen that the agreement between the two sets of results is good considering the present copolymers were prepared in solution at 60 °C, whereas those of Cowie *et al.* were prepared in bulk at 70 °C. Obviously, the polymerisation conditions did not play a great role in determining the polymer compositions.

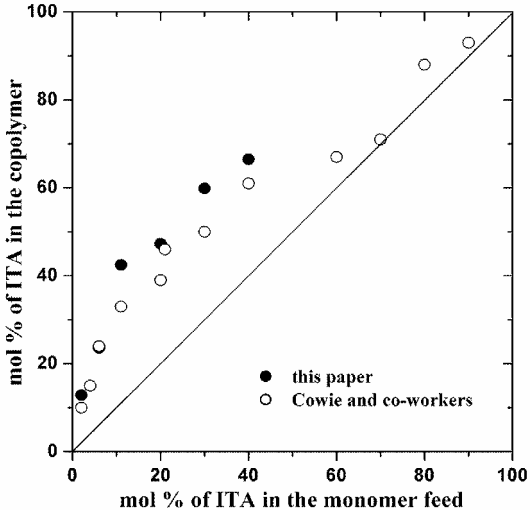
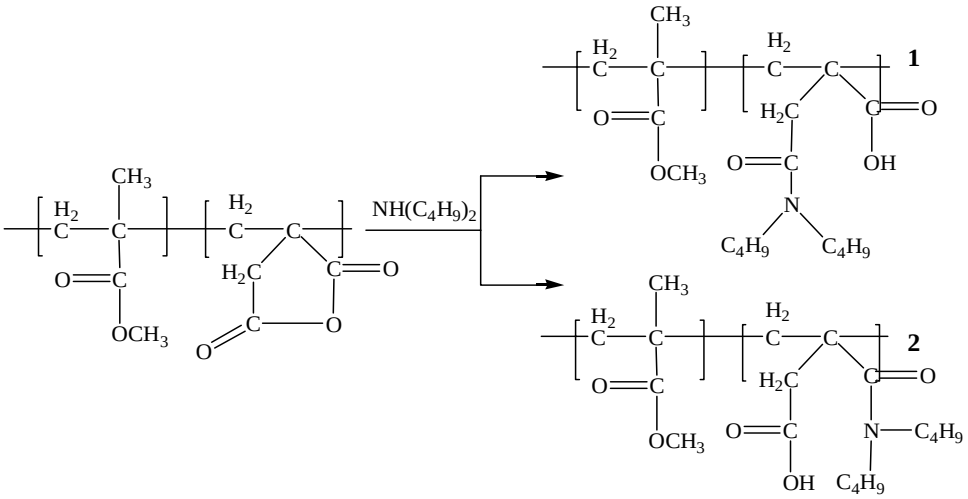


Fig. 1. Comparison of the compositions of ITA–MMA copolymers presented in this paper with the results of Cowie and co-workers.[12]

The copolymers of itaconic anhydride and methyl methacrylate were modified by amidation with di-*n*-butyl amine. The reaction between an amine and the itaconic anhydride units would be expected to yield two possible isomers (Scheme I).



Scheme 1. The reaction between di-*n*-butyl amine and an itaconic anhydride moiety in ITA–MMA copolymers.

It has been reported[13] that ring opening in the reaction of itaconic anhydride monomer and amines gives only the product with structure 1, although Galanti and co-workers presented evidence that trace quantities of isomer 2 are also produced.[14] The presence of small amounts of conjugated amide isomers was also reported by Hartford and co-workers.[15] Accordingly, a similar yield ratio of the two isomers obtained as the result of the amidation of itaconic anhydride units in the copolymers of ITA–MMA could be expected.

The IR spectra of the unmodified copolymers show carbonyl absorptions of the anhydride group at 1856 (ν_{sym}) and 1785 cm^{-1} (ν_{asym}). These peaks are characteristic of cyclic anhydride indicating that the polymerisation did not disrupt the itaconic anhydride moieties. The peak of the ester at 1733 cm^{-1} originates from methyl methacrylate. A comparison of the IR spectra of the modified with the unmodified copolymers (Fig. 2), shows the absence of the peaks characteristic of the anhydride group, and the appearance of absorption of the carbonyl amide group at 1634 cm^{-1}, which suggests that the amidation reaction went to completion.[16]

^{1}H-NMR Spectroscopy confirmed the results of the IR analysis. The ^{1}H-NMR spectra of the ITA–MMA copolymer with 30 mol % of ITA in the monomer feed before and after amidation are shown in Fig. 3. Differences can be seen in the presence of peaks at 3.65 ppm (the hydrogen from the methylene group in the anhydride ring) and 3.59 ppm (the hydrogens from the methyl ester group from methyl methacrylate). The peak at 3.65 ppm disappeared after reaction with di-*n*-butyl amine, indicating that the amidation went to completion.

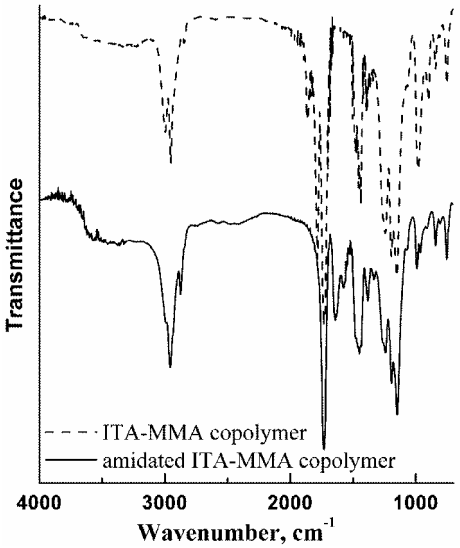


Fig. 2. IR Spectra of copolymer ITA–MMA with 6 mol % of ITA in the monomer feed before and after modification with di-*n*-butyl amine.

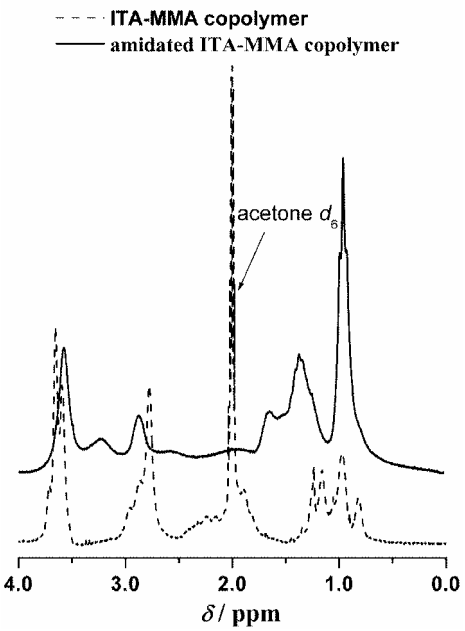


Fig. 3. ^{1}H-NMR Spectra of copolymer ITA–MMA with 30 mol % of ITA in the monomer feed before and after the reaction with di-*n*-butyl amine.

The compositions of the copolymers after modification by amidation with di-*n*-butyl amine were determined by elemental analysis *via* the nitrogen content in the copolymer. The molar percent of itaconamic acid in the obtained copolymers are given in Table II. It can be seen again that the amidation went to completion, which is in agreement with the results of ^{1}H-NMR and IR spectroscopy, and that the percent of amidation does not depend on the copolymer composition. A comparison of the copolymer compositions before and after modification is shown in Fig. 4.

The molar masses of the prepared copolymers after amidation were measured by GPC. The number average molar masses are plotted against the mol % of itaconic anhydride in Fig. 5, together with the polydispersity index.

As can be seen from Fig. 5, both the molar mass and the polydispersity of the resulting polymer decreased with increasing amount of itaconic acid in the monomer feed. Both facts could be consistent with the occurrence of chain transfer to monomer or additive in the monomer mixture. As the concentration of solvent was approximately constant in all polymerisations, one plausible explanation is that as well as being a comonomer, the itaconic anhydride could be a transfer agent (the chain transfer to methyl meythacrylate being very low[17]). It is well known that the chain transfer to monomer constant in the radical polymeri-

sation of di-*n*-alkyl itaconates is relatively high and two orders of magnitude higher than that of methyl methacrylate because of the presence of allylic hydrogens in the basic structure of itaconic acid-based monomers.[18]

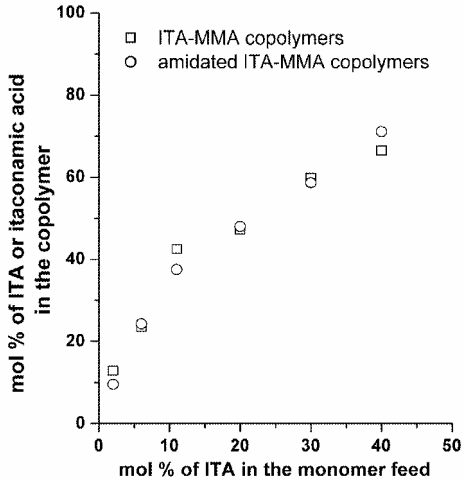


Fig. 4. Comparison of the compositions of ITA–MMA copolymers before and after amidation.

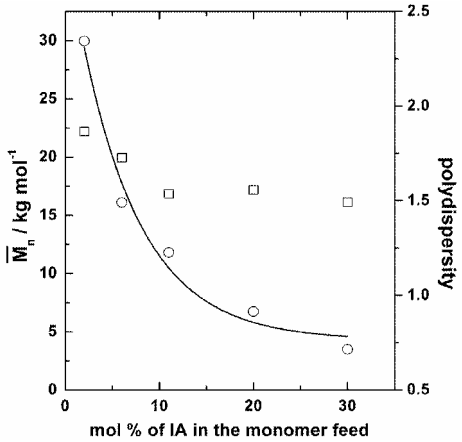


Fig. 5. Number average molar mass (○) and polydispersity (□) of the prepared copolymers as a function of the mol % itaconic acid in the monomer feed.

CONCLUSIONS

Copolymers of itaconic anhydride and methyl methacrylate were synthesised in solution at 60 °C. The determined monomer reactivity ratios are r_{ITA} = = 1.35±0.11; r_{MMA} = 0.22±0.22 (by the Fineman–Ross method) and r_{ITA} = 1.27± ±0.38; r_{MMA} = 0.10±0.05 (by the Mayo–Lewis method). The reactivity ratios are in agreement with literature values[12] for the copolymerisation of these monomers in bulk at 70 °C.

Chain transfer to itaconic anhydride occurred during the radical copolymerisations, limiting the molar masses of the polymers obtained from monomer feeds containing larger amounts of itaconic anhydride.

Amidation of the anhydride units in the copolymer with di-*n*-butyl amine gave itaconamic acid with complete conversion (confirmed by ^{1}H-NMR and IR spectroscopy and nitrogen analysis). The percent of amidation did not depend on the copolymer composition.

This method of modification of itaconic anhydride moieties in copolymers offers a convenient method of obtaining itaconamic acid-containing polymers without the difficulties generally experienced in the preparation of itaconamic acid monomers and in their direct polymerisation.

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И З В О Д

СИНТЕЗА И МОДИФИКАЦИЈА КОПОЛИМЕРА АНХИДРИДА ИТАКОНСКЕ КИСЕЛИНЕ И МЕТИЛ-МЕТАКРИЛАТА

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Испитивана је радикална кополимеризација анхидрида итаконске киселине и метил-метакрилата у раствору на 60 °C. Састав кополимера одређен је ^{1}H-NMR спектроскопијом и израчунати су односи реактивности мономера, r_{ITA} = 1.35±0.11; r_{MMA} = 0.22±0.22 (методом Фајнман–Рос) и r_{ITA} = 1.27±0.38; r_{MMA} = 0.10±0.05 (методом Мејо–Луис). Синтетизовани кополимери су модификовани реакцијом са дибутил-амином. Након амидације састав кополимера одређен је елементалном анализом на основу садржаја азота. Амидацијом анхидридних јединица у кополимерима дибутил-амином настале су комономерне јединице итаконамичне киселине.

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REFERENCES

1. T. Oishi, *Polym. J.* **12** (1980) 719
2. M. Urzua, A. Opazo, L. Gargallo, D. Radić, *Polym. Bull.* **40** (1998) 63
3. T. Otsu, H. Watanabe, J.–Z. Yang, M. Yoshioka, A. Matsumoto, *Makromol. Chem., Macromol. Symp*. **63** (1992) 87
4. A. V. Galanti, B. T. Keen, R. H. Pater, D. A. Scola, *J. Polym. Sci.* **26** (1981) 2243
5. T. M. Pyriadi, A. S. Berzinji, *Designed Monom. Polym.* **6** (2003) 115
6. K. Yokota, T. Hirabayashi, T. Takashima, *Makromol. Chem.* **176** (1975) 1197
7. W. Mormann, J. Ferbitz, *Eur. Polym. J.* **39** (2003) 489
8. T. Otsu, J.–Z. Yang, *Polym. Int* . **25** (1991) 245
9. A. V. Galanti, D. A. Scola, *J. Polym. Sci.* **19** (1981) 451
10. M. Fineman, S. D. Ross, *J. Polym. Sci.* **5** (1950) 259
11. F. Mayo, F. Lewis, *J. Am. Chem. Soc.* **66** (1944) 1594
12. A. F. Miles, J. M. G. Cowie, *Eur. Polym. J.* **27** (1991) 165
13. F. K. Beilstein, *Handbook of Organic Chemistry*, Vol. 17, Springer, Berlin, 1933, p. 442
14. A. V. Galanti. F. Liotta, B. T. Keen, D. A. Scola, *J. Polym. Sci*. **20** (1982) 233
15. S. L. Hartford, S. Subramanian, J. A. Parker, *J. Polym. Sci.* **16** (1978) 137
16. R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1974
17. *Polymer Handbook*, J. Brandrup, E. H. Immergut, Eds., 3rd Ed., Wiley, New York, 1989, p. II/85
18. S. L. Tomić, J. M. Filipović, J. S. Veličković, L. Katsikas, I. G. Popović, *Macromol. Chem. Phys.* **200** (1999) 2421.