

Polymerization of Itaconic Acid Initiated by a Potassium Persulfate/*N,N*-Dimethylethanolamine System

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ABSTRACT: The synthesis and characterization of poly(itaconic acid) (PIA) with a novel initiator/activator system is presented. The initiator in this system was potassium persulfate, whereas the activator was *N,N*-dimethylethanolamine (DMEA). PIA was synthesized in distilled water and in 0.1M HCl at 40°C with reaction times of 72 and 96 h. PIA was investigated with differential scanning calorimetry, gel permeation chromatography, and pulse gradient spin echo-NMR and compared to the same polymer synthesized in dioxane with 2,2'-azobisiso-

butyronitrile as the initiator. It was shown that, despite the fact that some residual DMEA remained in the system, the properties of the PIA polymerized in the aqueous phase were very similar to the dioxane-synthesized polymer, which will enable a faster, cheaper, and environmentally more acceptable polymerization of itaconic acid. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3275–3282, 2008

Key words: initiators; NMR; synthesis; water-soluble polymers

INTRODUCTION

Polymers of itaconic acid and its derivatives are viable alternatives to acrylic and methacrylic acid based polymers. The main advantage of itaconic acid today is that its production does not depend on petrochemical sources. Itaconic acid can be produced from a variety of agricultural products, for example, through the fermentation of molasses by *Aspergillus itaconicus*¹, *Aspergillus terreus*,² some strains of *Candida*,³ and *Ustilago*⁴ through the direct enzymatic conversion of citric acid,⁵ or even from starch.⁶ Its use is relatively widespread, and reviews by Tate⁷ and, more recently, Willke and Vorlop⁸ covered this topic in great detail.

The disadvantage for the more extensive application of poly(itaconic acid) (PIA) is its more time-consuming synthesis compared with polymers of acrylic and methacrylic acids, largely because of the increased size of the itaconic acid molecule. The main goal of this study was to explore the feasibility of a new polymerizing system that would shorten the time needed to obtain the polymer. Although PIA can be synthesized in various ways, for example, by the hydrolysis of PIA esters or poly(itaconic

anhydride),⁹ most routes involve the direct polymerization of itaconic acid, which may be performed in either various organic solvents or water-based systems.

Commonly used solvents include methanol and dioxane. Although these polymerizations have shown good results in terms of the polymer molecular weight and conversion, the polymerization times are long, typically on the order of weeks. For this study, we synthesized PIA in various solvents to compare them with water-based systems.

Itaconic acid is a water-soluble monomer, and hence, it seems natural to consider its polymerization in the aqueous phase. Water as a solvent for free-radical polymerization has gained more attention in recent years, as demonstrated, for example, by detailed investigations of methacrylic acid,¹⁰ acrylic acid,¹¹ and acrylamide.¹² The polymerization of itaconic acid in aqueous solution has been known for a long time because of the pioneering works of Marvell and Shepperd,¹³ who were the first to use a persulfate initiator in an acidic solution. However, the polymer they obtained was somewhat degraded, which indicated that the limiting factor in the polymerization of itaconic acid was the temperature. Monomer decarboxylation occurs at elevated temperatures; for example, polymerizations at 60°C yield a highly decarboxylated product.¹⁴ It is, thus, very important to keep the reaction temperature sufficiently low to prevent decarboxylation. Nagai and Yoshida¹⁵ investigated the pH dependence of the polymerization rate and concluded that the rate

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decreased with increasing pH and approached zero at pH = 12.5.

The presence of itaconic acid has been reported to facilitate the thermal decomposition of potassium persulfate (PPS or $K_2S_2O_8$).¹⁶ Persulfate has been used as a convenient initiator for itaconic acid polymerizations, with the standard initiator/activator system for water-based polymerization being $K_2S_2O_8/K_2S_2O_5$. There have also been recent reports of the use of $Na_2H_2PO_2$ as an activator,^{17,18} in which the authors have reported that sodium hypophosphite accelerated the thermal decomposition of PPS and thus reduced the temperature required for the formation of free radicals.

Water-soluble amino alcohols have been known to accelerate the polymerization of methyl acrylate.¹⁹ In this article, we report both the synthesis of PIA by a novel system with *N,N*-dimethylethanolamine (DMEA) as the activator and the properties of the obtained polymer. DMEA is a widely available and nonexpensive compound, and therefore, it is potentially suitable for large-scale production. In this respect, amino alcohols possess another advantage, as they can act as oxygen scavengers.²⁰ It has been shown that DMEA reduces the oxygen-induced polymerization inhibition period by up to 50%,²¹ which thus increases the robustness of the reaction.

EXPERIMENTAL

Itaconic acid (purity 99%+) was obtained from Acros Organics (Geel, Belgium). PPS and DMEA were purchased from Fluka (Buchs, Switzerland).

Polymerizations in aqueous media

The polymer was synthesized from a degassed 10 wt % solution of itaconic acid in either 0.1 mol of HCl or distilled water at 40°C for 72 h under a nitrogen atmosphere. The amount of initiator, PPS, was 5 mass % in all of the experiments, whereas the molar ratio of DMEA to PPS ranged between 0.04 and 1. The obtained polymers were precipitated in isopropyl alcohol and dried *in vacuo* to a constant mass. For each amount of DMEA, three samples were made, that is, 15 samples in 0.1M HCl and 9 samples in H_2O . The initial mass of itaconic acid was 2 g in each synthesis.

Polymerizations in organic solvents

To compare the rate of aqueous polymerization with polymerization in organic solvents, the polymerizations of itaconic acid in five different organic solvents with 2,2'-azobisisobutyronitrile (AIBN) as the initiator were also investigated, so the polymeriza-

tion of itaconic acid was carried out in five solvents: 1,4-dioxane, methanol, ethanol, 2-propanol, and 1-butanol. The monomer concentration was 1.00 mol/dm³ in all of the solvents used. The initiator (AIBN) concentration was 0.03 mol/dm³. Additional measurements were performed in 1,4-dioxane and 2-propanol with initial monomer concentrations of 0.7 and 0.85 mol/dm³.

All of the samples of PIA in organic solvents were synthesized with the same procedure: 10 mL of the solution of itaconic acid and AIBN in appropriate solvent were poured into a glass ampule. The solution was deoxygenated with bubbling nitrogen for 30 min, and the ampule was vacuum-sealed. The polymerization was carried out at 34°C. The polymer obtained was purified by repeated precipitation of a methanol solution with diethyl ether and was dried *in vacuo* at room temperature for 72 h. The PIA obtained was checked by NMR to ensure that no residual monomer or traces of solvent were present.

Characterization of the polymers

The polymers were characterized by viscometry, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), pulse gradient spin echo (PGSE)-NMR, and thermogravimetry (TG).

Viscometry was performed in methanol at 25°C with an Ubbelohde viscometer (Belgrade, Serbia). Molar masses were calculated with the Kuhn–Mark–Houwink–Sakurada equation:²²

$$[\eta] = 1.51 \times 10^{-3} \cdot M_w^{0.82}$$

where M_w is the weight-average molecular weight.

A Waters system (Milford, MA) was used for the GPC measurements with 0.1M $LiNO_3$ as the eluent, a pH of 8, 0.04M phosphate buffer with 0.02% NaN_3 at 35°C, a flow rate of 1 mL/min, a sample concentration of 1 mg/mL, and a loop volume of 200 μ L. Suprema columns (Polymer Standards Service, Mainz, Germany) were used and consisted of an 8 \times 50 μ m² guard and three columns (8 \times 300 mm²) with 10- μ m packing and pore sizes of 100, 1000, and 3000 Å. Detection by a differential refractometry detector (Waters DRI2410) was used. Effective calibration toward poly(acrylic acid) standards (Polymer Standards Service) was applied. Data were acquired and evaluated by means of WinGPC 7.2 software from Polymer Standards Service. The DSC measurements were performed with a PerkinElmer DSC 2 (Waltham, MA) under nitrogen at a heating rate of 10°C/min. TG measurements were carried out under nitrogen

at a heating rate of 10°C/min and a flow rate of nitrogen of 26 mL/min on a PerkinElmer TGS 2 instrument.

The PGSE-NMR measurements were performed on a Bruker AMX 360 high-resolution ^1H -NMR spec-

trimeter (Rheinstetten, Germany) with a stimulated echo sequence. Trapezoidal gradient pulses were generated with a Bruker constant-current gradient amplifier. The self-diffusion coefficient (D_s) was calculated according to eq. (1):²³

$$A(G, \delta) = A_0 \exp \left[-\gamma^2 G^2 \left(\frac{30\Delta(\delta + \sigma)^2 - (10\delta^3 + 30\sigma\delta^2 + 35\sigma^2\delta + 14\sigma^3)}{30} \right) D_s \right] \quad (1)$$

where A_0 is determined by the number of protons in the sample, γ is magnetogyric ratio of nucleus under observation in this case proton and $A(G, \delta)$ is the measured peak integral in the presence of gradient pulses of intensity G , duration δ , and ramp time σ over a diffusion timescale of Δ . All of the experiments were performed at 25°C.

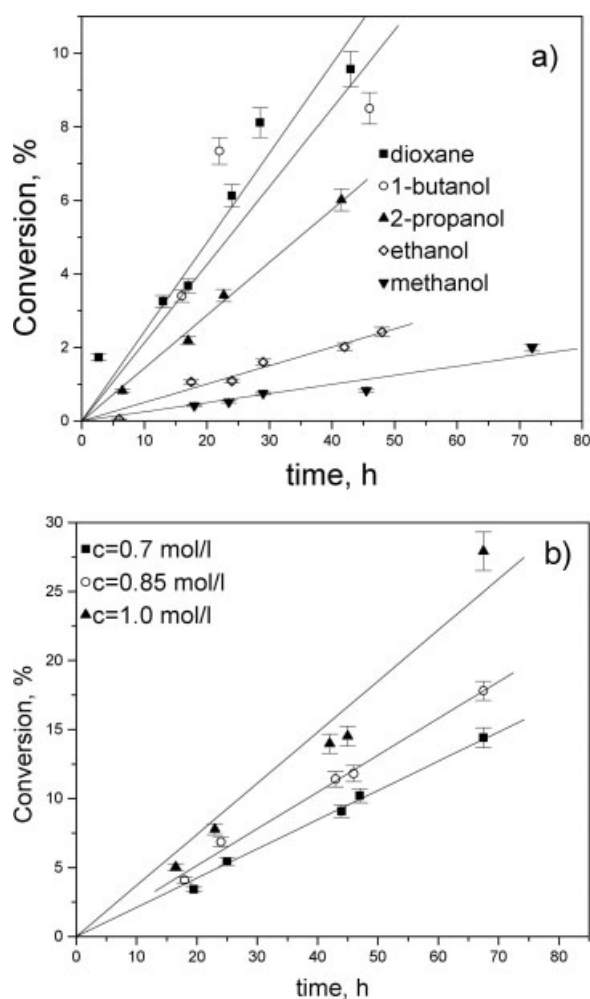


Figure 1 Conversion versus time for (a) the polymerization of IA in different organic solvents and (b) three monomer concentrations for the polymerization in dioxane.

RESULTS

Polymerization yields and molar masses obtained in the organic solutions

The polymerization yields in organic solutions are given in Figure 1. It was obvious that the yields for the same polymerization times in organic solvents were much lower than those of the aqueous polymerizations and that the fastest polymerization rate was observed in dioxane. For that reason, the dioxane-polymerized sample was used as the organic-solvent synthesized PIA that was used for comparison with the aqueous polymerized samples.

The samples' molar masses were calculated from viscometric data (for yields lower than 8%, there was not enough sample for acceptable measurements), and with regard to the polymerization time, there were no dramatic changes in the limiting viscosity number or molar mass with the change in polymerization time. On the other hand, the monomer concentration affected the limiting viscosity number and molar mass values of the obtained polymers. As the monomer concentration increased, the molar masses decreased, as expected. For the polymerization in dioxane, this is shown in Figure 2.

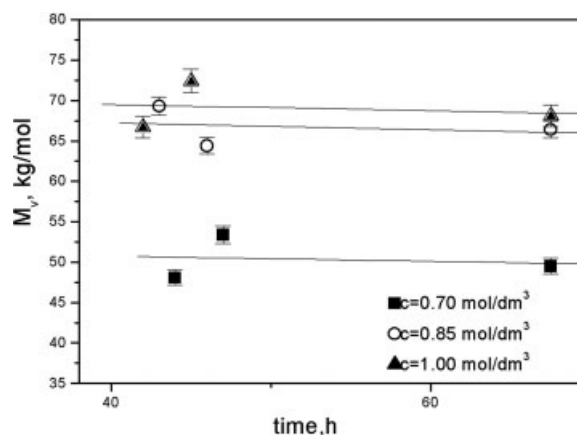


Figure 2 Molar masses of PIA synthesized in dioxane with different monomer concentrations, C.

TABLE I
Yields and Molar Masses of the Polymers
Synthesized in Organic Solvents

Monomer concentration (mol/L)	Polymerization time (h)	Yield (%)	M_v (mol/dm ³)
0.7	19.5	3.41	—
	25	5.43	—
	44	9.08	48.1
	47	10.2	53.4
	67.5	14.4	49.5
0.85	18	4.08	—
	24	6.85	—
	43	11.4	69.3
	46	11.8	64.4
	67.5	17.7	66.4
1.00	16.5	5.02	—
	23	7.77	—
	42	14.0	66.7
	45	14.5	72.4
	67.5	27.9	68.1

Summarized data on the yields and molar masses of the polymers synthesized in organic solvents are given in Table I.

Yields and molar masses obtained in the aqueous polymerizations

The polymer yields were independent of the amount of amine added. With a DMEA/PPS molar ratio of 0.04 to 1, the yields were about 50% after 72 h of polymerization at 40°C. Interestingly, the color of the isolated polymer was white when it was prepared in HCl, whereas the color of the polymer obtained in water was slightly pink, and this color remained even after repeated dissolution in water and reprecipitation from isopropyl alcohol.

The molar mass of PIA polymerized at the lower amounts of amine, between 0.04 and 1 mol/mol

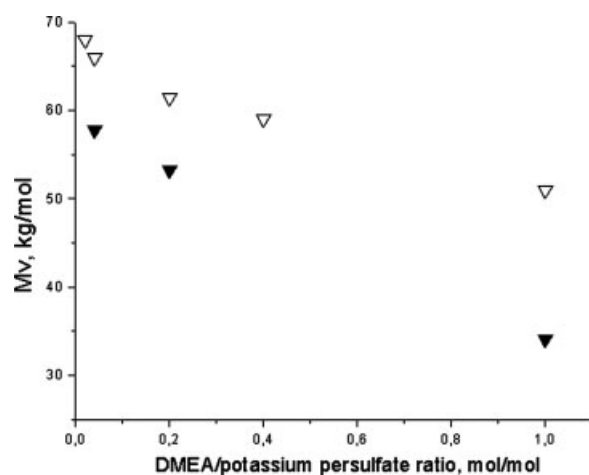


Figure 3 Influence of the amount of DMEA on M_v of PIA synthesized in (∇) 0.1M HCl and (▼) H₂O.

TABLE II
Molar Masses of PIA Synthesized in
0.1M HCl and Water

Sample	M_n (10 ⁻⁴ g/mol)	M_w (10 ⁻⁴ g/mol)	Polydispersity index
HCl/powder	4.70	8.77	1.87
HCl/film	4.83	9.69	2.00
Water/powder	2.33	4.34	1.86
Water/film	2.34	16.7	7.16 ^a

M_n = number-average molecular weight.

^a The sample was incompletely soluble.

DMEA/PPS, was characterized by viscometry. The variation in PIA molar mass with the amount of amine during the synthesis is presented in Figure 3.

The PIA samples synthesized with equal amounts of PPS and amine were isolated in two forms; that is, most of the polymer was obtained as a powder, but a thin transparent polymer film also formed on the walls of the precipitation vessel. The amount of

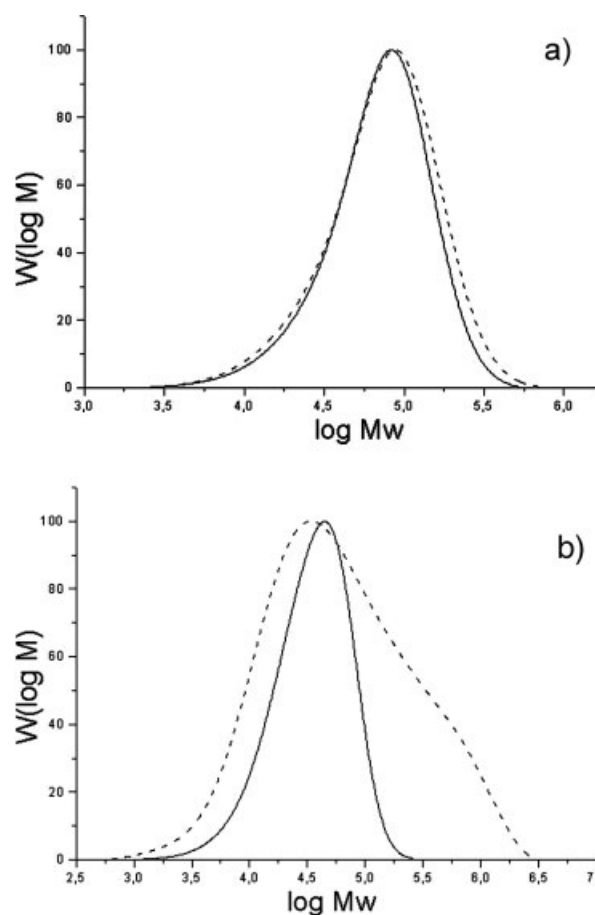


Figure 4 Molar mass distributions of PIA synthesized in 0.1M HCl (left) and water (right). The solid line represents the polymer powder, and the dotted line represents the polymer film. The initiation system was PPS/DMEA (1/1 mol/mol). W is a distribution function of molar mass, and M_w is a weight-average molecular weight.

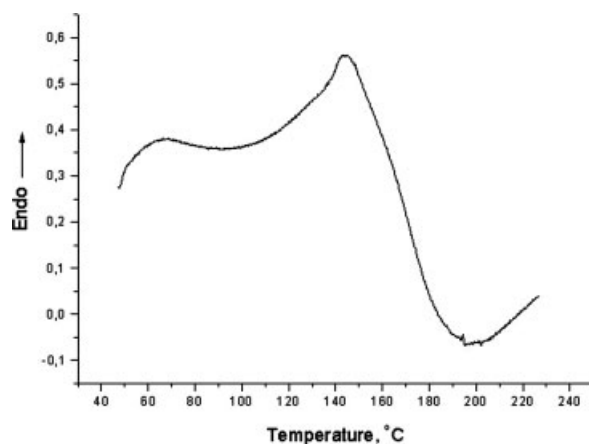


Figure 5 DSC trace of the PIA powder synthesized in water.

film varied between 10 and 15 mass % of the total yield. Both the film and the powder were investigated by GPC in the aqueous phase because the viscometry determination in methanol was ham-

pered because of their insolubility. The results of the GPC measurements are presented in Table II.

The most striking feature of these samples was the huge difference in the polydispersity index between the water-synthesized polymer film and the polymer powder (Fig. 4).

DSC

The DSC measurements were performed on HCl- and water-synthesized samples. The samples were characterized both as separated film and powder and as a sample in which the film and powder were not separated. For example, DSC of PIA synthesized in water is shown in Figure 5.

The peaks and shoulders were clearly distinguishable in the water-synthesized samples, whereas in the HCl-based samples, some peaks were not observed. Over 130°C, the degradation took place, which was confirmed by thermogravimetric analysis measurements, as discussed in the following paragraphs.

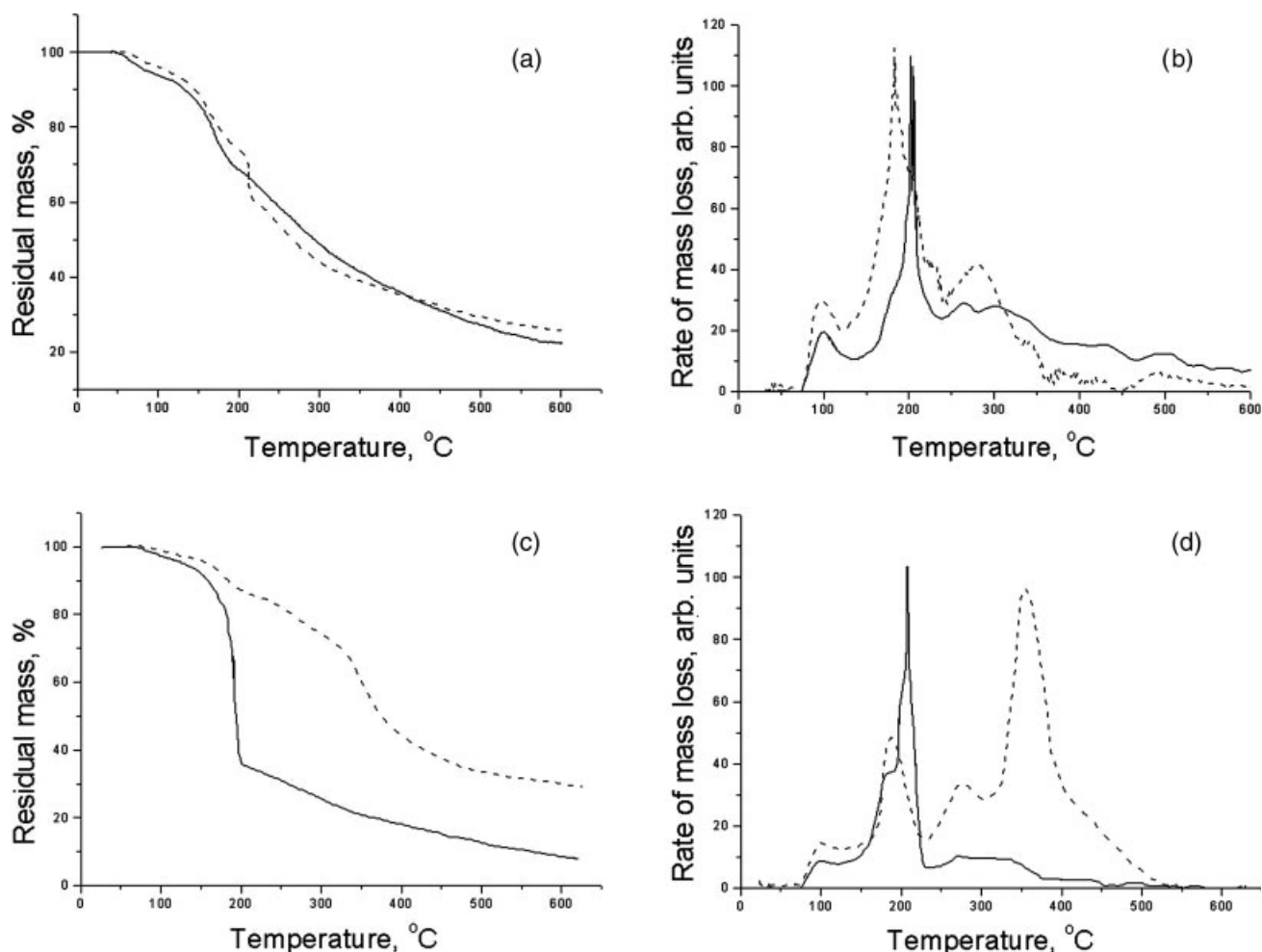


Figure 6 Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of PIA synthesized in 0.1M HCl (a) TG, (b) DTG, and water (c) TG, and (d) DTG. The solid line represents the polymer powder, and the dotted line represents the polymer film.

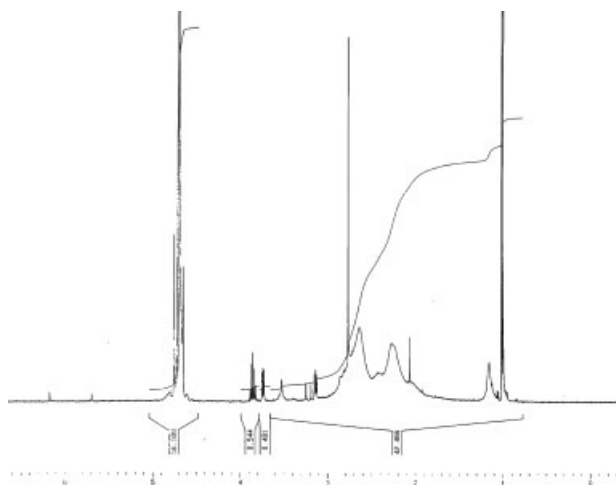


Figure 7 NMR of PIA synthesized with DMEA as the activator with the amine peak at 2.1.

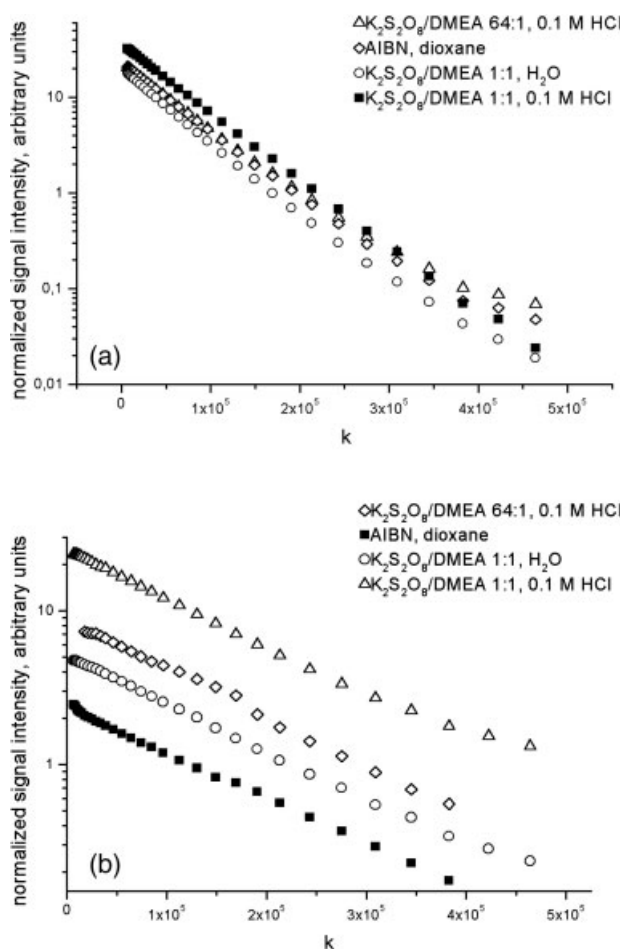


Figure 8 Typical PGSE-NMR dataset for water and PIA with a 10% polymer concentration. The synthesis was performed according to the routes described previously.

$$k = \gamma^2 G^2 ([30\Delta(\delta + \sigma)]^2 - (10\delta^3 + 30\sigma\delta^2 + 35\sigma^2\delta + 14\sigma^3))/30$$

TG

The only significant difference in the TG curves of the samples was seen in the film obtained from the water-synthesized polymer, whereas the other sample curves had a similar shape characteristic for PIA (Fig. 6).

Diffusion coefficients

The ^{13}C -NMR spectrum of the PIA synthesized in the presence of amine confirmed that some amine remained in the polymer, despite repeated precipitations (Fig. 7).

The diffusion coefficients were quantified from PGSE-NMR experiments. For monodisperse polymers, the attenuation plots should give a single-exponential relationship whose slope corresponds to D_s . The polydispersity results in upward curvature in the attenuation plot. The attenuation plots in this case only slightly departed from linearity, which showed that the polydispersity in these samples did not significantly affect the results. The representative attenuation plots are shown for 10% polymer solutions (Fig. 8).

The D_s values are shown as a function of polymer concentration. Water displayed a linear decrease of the diffusion coefficient with increasing initiator concentration in the solution of PIA synthesized with or without amine. The diffusion coefficients of PIA were significantly higher for samples prepared in the absence or at low levels of amine, especially for PIA concentrations of up to 5%. At 10% polymer concentration, the diffusion coefficients of PIA synthesized in water-based systems merged with the molar mass of the polymer, whereas they all were larger than the dioxane polymerized PIA (Figs. 9 and 10).

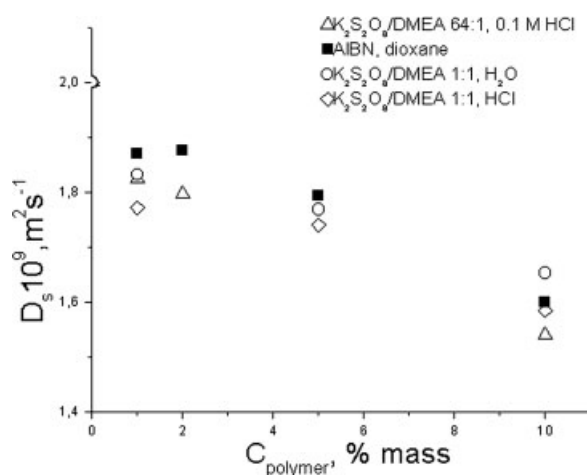


Figure 9 Diffusion coefficients of water in a D_2O solution of PIA synthesized with the routes described previously.

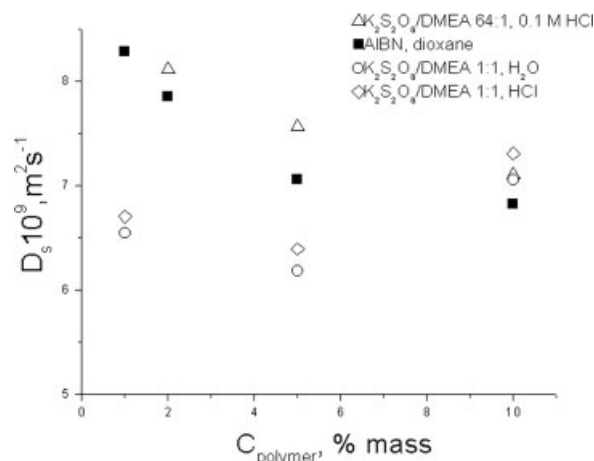


Figure 10 Diffusion coefficients of PIA in a D_2O solution synthesized in various ways with respect to the initiating system and reaction medium.

DISCUSSION

Our aim was to show that this novel synthesis of PIA could be presented as an appropriate method for a fast and efficient synthesis. Because of the use of nonexpensive reagents, this could be a good starting point for scaling up the reaction for industrial production of the polymer.

Both HCl and pure H_2O were used to evaluate the possibility of eliminating HCl in the process and thus making the reaction environmentally more acceptable. In pure H_2O , the polymer had a pink shade that probably originated from the residual amine. It is known that tertiary amines give a red color with dicarboxyl compounds. One of these reactions is even used for the colorimetric evaluation of tertiary amines.²⁴ Polymerization systems with amine were in its hydrochloride form; that is, when the synthesis was done in HCl, it yielded noncolored products,²⁵ and the same was observed in this study.

Another interesting point was that some of the polymer was obtained as a film. Although the film accounted for 10–15% of the total yield and did not present a significant part of the product, it showed some differences from the rest of the product obtained in the form of the powder.

The third difference in the dioxane-synthesized polymer was the insolubility of the polymer in methanol when a higher amount of amine was used during the synthesis.

It is most likely that the residual amine seen in the high-resolution NMR in the system was responsible for both effects and, as Tsuchida²⁶ showed for a similar system, polymers with carboxylic groups can form a soluble or insoluble complex with amine groups, depending on the order in which the groups

interact. We suspect that, in our case, both possibilities were present, which gave two somewhat different products and held the polymeric chains together with enough strength to prevent dissolution by methanol, with only the addition of water enabling dissolution. The polymer film obtained from the water-based synthesis was not completely soluble. It is known that itaconic polymers always retain some amount of amine, which cannot be removed, even after repeated precipitations with HCl solution.²⁷

The largest difference between the products was observed for the sample synthesized in pure water, where the film sample showed a very large polydispersity index, probably because of the amine holding the shorter chains together even in solution. The higher molar masses obtained in HCl were probably the result of the different pH values of the reaction medium, which is known to influence the polymerization, as previously mentioned.¹⁵

Apart from these differences, the investigations, for example, DSC, showed that there were no great differences between the samples. The features observed can be explained in the following way. The shoulder observed at temperatures around 130°C was already the onset of the degradation of the polymer, so the glass-transition temperature, expected to appear in this region, could not have been confirmed. The shoulder around 170°C was attributed to a small amount of residual itaconic acid that remained in the polymer. Similarly, the thermogravimetric curves showed the usual PIA trace, except for the pure water-synthesized film sample, which had a higher thermal stability, which probably due to the additional bonds with the amine, but this phenomenon will be further studied.

The PGSE-NMR data for the reduced diffusion coefficients of water showed that they decreased in a linear fashion with increasing polymer concentration, which indicated that obstruction effects governed their decrease. The results were of a similar magnitude for the HCl samples and the dioxane sample. A slight difference was noticed in the behavior of the sample that was synthesized in pure water. The decrease in its diffusion coefficient as a function of increasing polymer concentration showed a departure from a straight line. That could mean that obstruction effects were not the only ones governing the decrease in the diffusion coefficient. This effect could again probably be attributed to residual amine interactions in the polymer. We could not establish any significant connection between the polymer molecular weights and the diffusion coefficients of either polymer or water.

With the decrease in the diffusion coefficients of the polymer itself, it was clear that the PIA polymers synthesized with a larger amount of amine acted in a similar way, whereas the sample without and with

a very small amount of amine made another pair of similar traces. With increasing polymer concentration, the diffusion coefficients tended to converge. Such behavior was probably the result of a very small amount of residual amine in the system, where its specific effects could only be seen in very dilute solution, whereas in more concentrated solutions, obstruction effects predominated and yielded similar values, which were seen at a concentration of 10% concentration.

CONCLUSIONS

This investigation showed that the polymerization of itaconic acid with a $K_2S_2O_8$ /DMEA system can be a feasible starting system for PIA production. Although there was some residual amine present in the system that could not have been removed by standard purification, it was shown that it did not significantly alter the properties of PIA. The polymerization times were relatively short and gave good yields at a polymerization temperature that was low enough to prevent degradation, which is known to be a problem in itaconic acid polymerizations. Further investigations will show if other amino alcohols increase the efficiency of this polymerization in terms of reaction times, product yields, and polymer properties.

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