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STUDY OF THE POLIMERIZATION OF METHACRYLIC ACID METHYL ESTER IN AN IONIC LIQUID MEDIUM

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ABSTRACT

This study explores the radical polymerization of methacrylic acid methyl ester in ionic liquids derived from formic acid and diethylamine or morpholine. Investigating the impact of various factors, including initiator type, concentration, and polymerization conditions, we highlight the influence on monomer conversion and resulting polymer characteristics. The findings underscore the potential for precise regulation of polymethyl methacrylate properties through the selection of ionic-liquid solvents and reaction conditions. The study concludes by emphasizing the synthesis of polymethyl methacrylate with a narrow polydispersity index in an ionic liquid environment based on morpholine and formic acid.

Keywords: polymethyl methacrylate, ionic liquids, radical polymerization, methacrylic acid methyl ether, formic acid, diethylamine, morpholine.

Introduction

As is known polyacrylates are one of the well-studied and accessible polymers that have found wide application in various fields of industry, from medicine to building structures. One of the well-known acrylic polymers is polymethyl methacrylate (PMMA), which is known as organic glass and is in demand in lighting engineering, medicine, aircraft and mechanical engineering.

This polymer is known as a high-molecular compound that has good chemical resistance, successfully combines rigidity, density and impact strength, and the main areas of application of polymethyl methacrylate are determined by its main quality - high transparency[1, 2].

At the current stage of macromolecular chemistry development, the exploration of novel, efficient, and environmentally friendly approaches to well-known polymers is highly relevant and extensively investigated. The incorporation of new catalytic systems and reaction media into polymer chemistry plays a crucial role in addressing this challenge. In recent years, ionic liquids (ILs) have been actively employed as alternatives to conventional solvents in both organic reactions and polymer synthesis [3-5].

In this regard, we carried out a study of the radical polymerization of methacrylic acid methyl ester (MAME) in the environment of ionic liquids based on formic acid and diethylamine or

morpholine. The influence of the ratio of ionic liquid to methacrylic acid methyl ester, the concentration and nature of the radical initiator (benzoyl peroxide (BP), cumene hydroperoxide (CHP)), as well as temperature and polymerization duration on the conversion of methacrylic monomer and the molecular weight of the resulting polymer was studied.

Experimental part

Polymerization of methacrylic acid methyl ester in the environment of synthesized ionic liquids was carried out by a radical mechanism.The process was carried out in sealed glass ampoules in an inert environment. For this purpose, the corresponding ionic liquid was loaded into a glass ampoule and, in order to remove air entrained in the liquid, the system was degassed by vacuuming at room temperature for 20 minutes. Then a methacrylic monomer with a calculated amount of a radical initiator pre-dissolved in it was added to the ionic liquid. After repeated freezing and vacuuming, the ampoule was sealed and placed in a thermostat. For comparison, the polymerizations of the indicated methacrylic acid esters were carried out under similar conditions in an organic solvent – benzene.

Depending on the nature of the ionic liquid used as the reaction medium, the polymerization process of methacrylic acid esters occurs in a homogeneous or heterogeneous phase. In the case of the process occurring in a heterogeneous phase, the separation of the resulting polymer from the unreacted part of the monomer, as well as the solvent - ionic liquid, was carried out by conventional filtration. And in the case of the process occurring in a homogeneous phase, the resulting polymers were isolated by precipitation from benzene solutions in ethanol. To remove the remnants of the unreacted part of the monomer, as well as the ionic liquid used as the reaction medium, the isolated polymer mass is washed with ethyl alcohol.

Results and discussion

Polymerization of methacrylic acid methyl ester in an ionic liquid medium - diethylammonium formate. The studies carried out have established that the polymerization of MAME in the ionic-liquid medium diethylammonium formate, as well as the polymerization of BMA [6], occurs in a heterogeneous environment, with the resulting polymer precipitating. For all studied ratios of monomer to ionic liquid (1.0: 0.5 - 2.0 wt) for 10 hours of polymerization, the polymer yield ranges from 87.4-98.0% wt (Table 1). Thus, with a weight ratio of monomer: ionic liquid of 1:2 (solution concentration - 33% wt), a polymerization temperature of 80^{o}C, the amount of radical initiator BP of 0.2% wt and a reaction duration of 10 hours, the yield of polymethyl methacrylate is 89.9% wt. Under other identical conditions, with an equal weight ratio of monomer and ionic liquid (solution concentration 50% wt) - 87.4 wt%, and at a weight ratio of 1:0.5 wt (solution concentration 67.7% wt), as in the case of polymerization of butyl methacrylate, the maximum yield of polymethyl methacrylate is observed - 98% of the mass. With an increase in the initiator concentration to 0.5%, at equal weight ratios of monomer and ionic liquid, the conversion of the monomer increases significantly and the yield of the polymer product after 10 hours of polymerization is 98% by weight.

A study of the influence of the nature of the initiator on the polymerization process showed that during the polymerization of methyl methacrylate with the participation of a radical initiator - CHP in the environment of the specified ionic liquid, a relatively low polymer yield is observed, compared to polymerization in the presence of BP under identical conditions. Thus, with an equal mass ratio of monomer to ionic liquid and a CHP concentration of 0.5%, the polymer yield is only 52%, while under identical conditions using the radical initiator BP, the polymer yield was 98% (Table 1).

Table 1. Polymerization of MMA in an ionic liquid medium based on formic acid and diethylamine

MMA: IL	Initiator,%		T^0C	Duration of polymerization, h	Yield, %mass	Characteristic viscosity	Average molecular weight
	BP	CHP					
1:0.5	-	0.2	130	10	58.14	0.42	136000
1:1	-	0.5	130	10	52.59	0.32	94000
1:2	-	0.2	130	10	56.7	0.38	112000
1:0.5	0.2	-	80	10	98.0	1.53	726000
1:1	0.5	-	80	10	98.0	1.05	447000
1:1	0.2	-	80	10	87.4	1.21	523000
1:2	0.2	-	80	10	89.8	1.38	538000

In this case, the polymethacrylate obtained with the participation of CHP as an initiator, depending on the reaction conditions, was characterized by a significantly low molecular weight (94000-136000) compared to the polymethacrylate obtained under identical conditions with the participation of BP as an initiator (447000 - 726000). These data may be related to the temperature condition of polymerization, since with the participation of CHP, polymerization was carried out at relatively high temperatures – 130°C, where, apparently, along with initiated polymerization, thermal polymerization also takes place.

Polymerization of methyl methacrylate in an ionic liquid medium - morpholinformate. In the case of the polymerization of MAA in the ionic liquid morphoformate, despite the fact that the process from beginning to end proceeds under homogeneous conditions with the formation of transparent solid solutions, the same patterns are observed. With increasing monomer concentration in the ionic liquid medium, initiator concentration and polymerization time, the yield of polymethyl methacrylate increases. Thus, with an equal weight ratio of monomer to ionic liquid, concentration of the BP initiator equal to 0.2% by weight, polymerization time of 10 hours, the yield of polymethyl methacrylate is 86.9% by weight, and with an increase in the polymerization time to 15 hours, the yield of the polymer under the same conditions increases and amounts to 97.25% of the mass.

If we take into account that the resulting polymer product is released by precipitation, then the obtained value of the polymer yield indicates almost complete conversion of the monomer under the specified polymerization conditions. With an increase in the concentration of the radical initiator benzoyl peroxide to 0.5% by weight, almost complete conversion of the monomer into a polymer product is observed with a polymerization time of 10 hours and the yield of polymethyl methacrylate is 99.0%.

Table 2. Polymerization of MMA in an ionic-liquid medium – morpholinformate.

MMA: IL	BP initiator, %	T^0C	Duration of polymerization, h	Yield, %	Characteristic viscosity, dl/g	Average molecular weight
1:1	0.2	80	10	86.9	2.29	1231000
1:1	0.2	80	15	97.25	2.31	1253040
1:2	0.2	80	10	89.76	1.26	565000
1:4	0.2	80	10	80.62	1.47	692000
1:1	0.5	80	10	99.0	2.03	1053000

A study of the influence of the monomer concentration in the ionic liquid on the

polymerization process showed that, under other identical polymerization conditions at a polymerization temperature of 80° C and a polymerization duration of 10 hours, an initiator concentration of 0.2% by weight with an increase in the ratio of ionic liquid to monomer by 4 times, that is, dilution of the reaction medium (solution concentration 20% wt), the polymer yield decreases and amounts to 80.62% wt, compared to the polymer yield (86.9%) at a solution concentration of 50% wt., which is associated with an increase in the viscosity of the solution during polymerization in ionic -liquid environment.

Conclusion

Analysis of the results obtained suggests the possibility of regulating the molecular weight and molecular weight distribution of polymethyl methacrylate by selecting an ionic-liquid solvent, as well as reaction conditions. Detailed studies have revealed that polymethyl methacrylate with a relatively narrow polydispersity index can be synthesized by carrying out the polymerization process of methyl methacrylate in an ionic liquid environment based on morpholine and formic acid, with a monomer concentration in the initial mixture of 33% wt.

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METAKRİL TURŞUSUNUN METİL EFİRİNİN İON MAYE MÜHİTİNDƏ POLİMERLƏŞMƏSİNİN TƏDQİQİ

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XÜLASƏ. Tədqiqat işində qarışqa turşusu və dietilamin və ya morfolin əsasında sintez edilmiş ion mayelərində metakril turşusunun metil efirinin radikal polimerləşməsi tədqiq edilmişdir. Metilmetakrilatın ion maye mühitində polimerləşmə prosesinə müxtəlif amillərin, o cümlədən ion maye həlledicinin təbiəti, monomerə nisbətinin, temperaturun, inisiatorun təbiəti və miqdarının, polimerləşmə müddətinin təsiri tədqiq olunmuşdur. Aparılan tədqiqatlar nəticəsində müəyyən edilmişdir ki, ion-maye həlledicilərin və reaksiya şəraitindən asılı olaraq alınmış polimetilmetakrilatın xassələrini tənzimlənmək mümkündür. Belə ki, morfolin və qarışqa turşusu əsasında ion maye mühitdə alınmış polimetilmetakrilat dar polidisperslik indeksi ilə xarakterizə olunurlar.

Açar sözlər: polimetilmetakrilat, ion mayeləri, radikal polimerləşmə, qarışqa turşusu, dietilamin, morfolin

ИЗУЧЕНИЕ ПОЛИМЕРИЗАЦИИ МЕТИЛОВОГО ЭФИРА МЕТАКРИЛОВОЙ КИСЛОТЫ В ИОННО-ЖИДКОСТНОЙ СРЕДЕ

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АБСТРАКТ. В представленном материале приведены результаты исследований радикальной полимеризации метилового эфира метакриловой кислоты в среде ионных жидкостей на основе муравьиной кислоты и диэтиламина или морфолина. Изучено влияние соотношения ионной жидкости к метилметакрилату, концентрации и природы радикального инициатора, а также продолжительности полимеризации на конверсию метакрилового мономера. Полученные данные указывают на возможность регулирования свойств полученного полимера посредством выбора ионно-жидкостной среды и условий реакции. Так, полиметилметакрилат полученный в ионно-жидкостной среде на основе морфолина и муравьиной кислоты характеризовался с узким индексом полидисперсности.

Ключевые слова: полиметилметакрилат, ионные жидкости, радикальная полимеризация, муравьиная кислота, диэтиламин, морфолин.