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# $^{60}$Co γ-irradiation initiated polymerization in ionic liquids – The effect of carbon-chain length of monomer

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**Abstract**

Gamma-radiation initiated polymerization of Methyl methacrylate (MMA) and Butyl methacrylate (BMA) was carried out in room temperature ionic liquid (RTIL) $[Me_3NC_2H_4OH]^+$ $[ZnCl_3]^-$ and RTIL/organic solutions. MMA and BMA were selected as the represents of vinyl monomers in order to understand the effect of side-chain carbon length on properties of the resulting polymer. Although both PMMA and PBMA from RTIL/organic solution at high RTIL content have significantly higher molecular weight than those at RTIL 20 vol.%, their molecular weight distributions (MWDs) are clearly different. For polymerization in RTIL/THF and RTIL/MeOH solutions, PMMA has a single-modal MWD while PBMA has a multi-modal MWD. This difference is probably due to the better compatibility of PMMA with RTIL/THF and RTIL/MeOH solutions, though PMMA is insoluble in pure methanol.


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## 1. Introduction

The new class of room temperature ionic liquids (RTILs) emerged in the early of 1980s. Due to the potential advantages in commercial applications and environmental protection, RTILs have attracted ever-increasing interests in recent years. Ionic liquids are known for their non-volatility and high polarity, and most of them are non-toxic and easily recycled, etc. [1–3].

Owing to their unique properties, application of room temperature ionic liquids as reaction media for polymerization may offer some other advantages [4]. For example, ionic liquid can be used as the solvent for both monomer and catalyst in cationic polymerization [5] and in atom transfer radical polymerization (ATRP) [6,7]. The resulting polymer can be separated from the residual catalyst by extraction and the ionic liquid/catalyst system

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may be recovered. Various polymerizations have been studied using room temperature ionic liquids as media in common reaction routes, including radical polymerization, ionic and coordination polymerization, polycondensation, polyaddition, electrochemical polymerization and living/controlling polymerization (ATRP, RATF) [1,8–13].

RTIL is an important class of liquids and radiation effects in such liquids may attract the interest of radiation chemists and engineers. Up to now, however, very few groups have investigated the radiation-induced processes in room temperature ionic liquids. Allen et al. [14] studied the radiochemical stability of room temperature ionic liquids under gamma and electron beam irradiation because ionic liquids may be applied in the recycling of nuclear fuel. Wishart and Neta [15] and Marcineket et al. [16] invesitgated the transient species formed in ionic liquids by pulse radiolysis. We initiated a program to investigate radiation polymerization in RTIL with the aim to know the effect of ionic liquid on the resulting polymers' molecular weight, molecular weight distribution (MWD), yield, etc. In this article, radiation polymerization of two acrylate monomers (MMA: methyl methacrylate and BMA: butyl methacrylate) in RTIL/solvent/monomer systems was carried out to understand the effect of the monomer length on polymerization process, because these two monomers have a similar chemical structure but different side-chain carbon length. Tetrahydrofuran (THF) and ethanol (MeOH) were used to tune the ionic liquid property. A clear difference in molecular weight and MWD was identified between the polymerizations of the two monomers.

## 2. Experimental

A quaternary ammonium based ionic liquid, $[Me_3NC_2H_4OH]^+[ZnCl_3]^-$, is prepared according to the method described in the literature [17]. The molar ratio of choline chloride to $ZnCl_2$ is 1:2. In all cases, 5.0 vol.% newly distilled monomer (MMA, BMA) was added into the ionic liquid or the RTIL/organic (THF or MeOH) mixture. After bubbling $N_2$ gas to remove the air, samples (about 4.0 mL) sealed in glass ampoules were subjected to $^{60}Co$ rays from the cobalt-60 source in Shanghai Institute of Applied Physics, exposed to a total dose of 5 kGy at a dose rate of 5.3 Gy/min. The resulting polymers were separated by dropping slowly the irradiated samples into an excess amount of cooled methanol and by drying the precipitated product at 60 °C for 24 h under vacuum. Gel permeation chromatography (GPC) is used to analyze the molecular weight and MWD; eight standard polystyrene samples were used for calibration. GPC measurements were carried out in THF (flow rate: 1.0 mL/min) at 35 °C, using a Waters pump and a differential refractive index detector. Fluorescence spectra of the RTIL/organic system were taken on a Hitachi-FL4600 spectrofluorimeter.

## 3. Results and discussion

The used ionic liquid is miscible with vinyl monomers and many polar organic solvents, and forms a homogenous solution. In our previous work [18], we carried out copolymerization of MMA and styrene in the ionic liquid $[Me_3NC_2H_4OH]^+[ZnCl_3]^-$ and its mixture with THF and found that the polymerization proceeds by the radical mechanism. Here we investigate the polymerization of MMA and BMA in $[Me_3NC_2H_4OH]^+[ZnCl_3]^-$ and its mixture with THF and MeOH. Since the two polymers, PMMA and PBMA, are soluble in THF and insoluble in MeOH, the use of RTIL/TFH and RTIL/MeOH as polymerization media may result in significant difference in polymer properties.

### 3.1. Polymerization in RTIL/THF mixture

Fig. 1 shows the GPC traces of PMMA and PBMA obtained in the RTIL/THF mixed solvent at the same dose. It is seen that for both PMMA and PBMA the molecular weight increases rapidly with increasing the RTIL fraction in RTIL/THF mixture. However, the change of MWD with RTIL/THF ratio is clearly different for PMMA and PBMA. PMMA tends to remain a relatively narrow single-modal distribution by changing the RTIL fraction from 20 vol.% to 100 vol.%, while