

UNIVERSITI TEKNOLOGI MARA

**EFFECTS OF IONIC LIQUID
PROPERTIES ON THE SYNTHESIS
OF NEW FLEXIBLE ACRYLATES
VIA IN SITU FREE RADICAL
POLYMERISATION**

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ABSTRACT

Poly (methyl methacrylate) (PMMA) is one of the polymer host that exhibit stability towards lithium electrode. This is achieved when it is prepared in film form. Unfortunately, most PMMA films are brittle due to their polar nature which tends to form hydrogen bonds between the polymer chains. Therefore, various modifications have been made to improve the brittleness of this PMMA electrolyte film, such as mixing with another polymer, adding plasticizers, organic fillers or ionic liquid (IL). However, these can slightly improve the brittleness and ionic conductivity of PMMA. Therefore, modified PMMA was synthesized to obtain a flexible film by adding IL at the initial stage of polymerization, so that the formation of hydrogen bonds between PMMA chains can be hindered and thus a more flexible PMMA-based film can be obtained. This can be carried out via Free Radical Polymerization (FRP) technique. However, not all FRP polymerizations of PMMA with IL have been successful. Sometimes solid PMMA cannot be obtained from the polymerization, so no PMMA film can be produced. Unfortunately, the factors leading to these failures were not discussed in detail. Most of the studies reported that the viscosity of IL is the main reason for the failure of polymerization. Therefore, in this study, in addition of investigating the effects of viscosity, other properties, i.e., density, cation structure, molecular weight, polarity, self-diffusion coefficient and thermal decomposition were also investigated and discussed in detail. For this purpose, three ILs with similar anions, namely, 1-methylpentamethyldisiloxy-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [(SiOSi)₂C₁C₁pyrr][NTf₂] (IL1), 1-methyl-1-heptamethyltrisiloxymethylpyrrolidinium bis(trifluoromethylsulfonyl)imide [(SiO)₂SiC₁C₁pyrr][NTf₂] (IL2) and bis(pentamethyldisiloxymethyl)imidazolium bis(trifluoromethylsulfonyl)imide, [(SiOSiC₁)₂im][NTf₂](IL3) were selected. The results obtained were compared with other studies using 1-methyl-3-pentamethyldisiloxymethylimidazolium bis(trifluoromethylsulfonyl)imide [(SiOSi)₂C₁im][NTf₂] (ILR) consisting of a similar anion to support the arguments. It has been shown that the synthesis of MMA in IL depends not only on the viscosity, but also on the other factors mentioned above, especially the density and the size of the IL cation. Moreover, the presence of groups that can be attacked by the initiator should be avoided. As a result, only IL1 with the shorter cation size showed good compatibility and produced new transparent and solid PMMAIL1 (~28000 gmol⁻¹) with better thermal stability than the pure PMMA due to the strong PMMA-IL1 interaction. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) analyses proved that the IL1 was successfully incorporated into the PMMA matrix. FTIR and XRD analyses confirmed that inter-chain crosslinking via hydrogen bonding between the PMMA chain was minimized in PMMAIL1, as the bulky structure of IL1 occupied the space between the polymer chains. This concentration was found not sufficient to reduce the massive hydrogen bonds between PMMA chains. Therefore, the properties of PMMAIL1 were further improved when the IL1 concentration was increased to 20% (PMMA20IL1). A more flexible, freestanding film with higher ionic conductivity (~10⁻⁸ Scm⁻¹) and thermal stability than the pure PMMA (PMMAIL0) film was obtained from this PMMA20IL1 film. The ionic conductivity of this PMMA20IL1 film was increased to ~ 10⁻⁷ Scm⁻¹ by the addition of 5% lithium triflate (LiTf) salt, (PMMA20IL1S5) and does not obeys the Arrhenius rule. The system is consistent with OLPT (overlapping large polaron-tunelling) model.

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