Synthesis of chlorinated polypropylene grafted poly(methyl methacrylate) using chlorinated polypropylene as macro-initiator via atom transfer radical polymerization and its application in lithium ion battery

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ARTICLE INFO

ABSTRACT

Chlorinated polypropylene grafted poly(methyl methacrylate) (CPP-g-PMMA) was successfully synthesized using AlCl$_3$/FeCl$_2 \cdot 4H_2O$/triphenylphosphine (PPh$_3$) as catalyst and CPP as macro-initiator for the first time. Kinetics study revealed that the grafting reaction was consistent with the characteristic of atom transfer radical polymerization (ATRP). The effect of AlCl$_3$, as activator on the ATRP of MMA, was investigated and a possible polymerization mechanism was proposed. Finally, the CPP-g-PMMA membranes were assembled into batteries. The ionic conductivity and charge–discharge capacity of the membranes were investigated. It was found that the electrochemical performance of the graft products was better than that of CPP, which can be ascribed to the graft PMMA.

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1. Introduction

Polyolefins, such as polypropylene (PP) and polyethylene (PE), are often used as separator for lithium-ion batteries [1]. However, the poor affinity with electrolyte decreases their performances. Introducing polar functional groups into polyolefin, such as surface chemical modification [2] and surface coating [3], can enhance the affinity with electrolyte. However, surface chemical modification usually results in pore blocking [4]. For surface coating [5], the poor binding power between the coating and supporting layer makes the coating layer impermanent. Graft copolymerization offers an effective approach for incorporating specific properties into a material while retaining properties of the parent polymer [6]. ATRP is a suitable method to prepare graft copolymers due to the advantages of no homo-polymerization and the controllable characteristic. ATRP relies on the equilibrium between initiating species and radicals that are produced by the cleavage of the C–X bond by a redox-active, low-oxidation-state metal complex. Therefore, halogens should be first introduced into polyolefin if another component was grafted. However, some commercial halogen-containing polyolefins, such as chlorinated polypropylene (CPP) and poly (vinyl chloride) (PVC), cannot initiate ATRP effectively because they just contain inactive secondary C–Cl [7].

In this paper, the graft products of CPP-g-PMMA were successfully synthesized via ATRP using CPP as macro-initiator and AlCl$_3$ as activator for the first time. The controllability of the polymerization was verified and the activation-initiation-polymerization mechanism was proposed. Moreover, considering the potential application in lithium ion battery, the electrochemical performance of the graft polymer was also measured.

2. Experimental

CPP ($M_n = 35,000$ g/mol, Yancheng Huabang Chemical Co. Ltd., PR China), and AlCl$_3$ were dried in a vacuum oven before use. MMA (> 99%) was washed with sodium hydroxide (5 wt%), by washed with deionized water until neutralization. It was stored at -18 °C after dried over anhydrous magnesium sulfate, distilled under reduced pressure [8]. PPh$_3$, FeCl$_2 \cdot 4H_2O$ and N-methy-2-pyrrolidone (NMP) were used as received. CPP was dissolved in NMP at 80 °C for 1.5 h. The solution was aged for 2 h at designed temperature after AlCl$_3$ was added. FeCl$_2 \cdot 4H_2O$, PPh$_3$ and MMA were
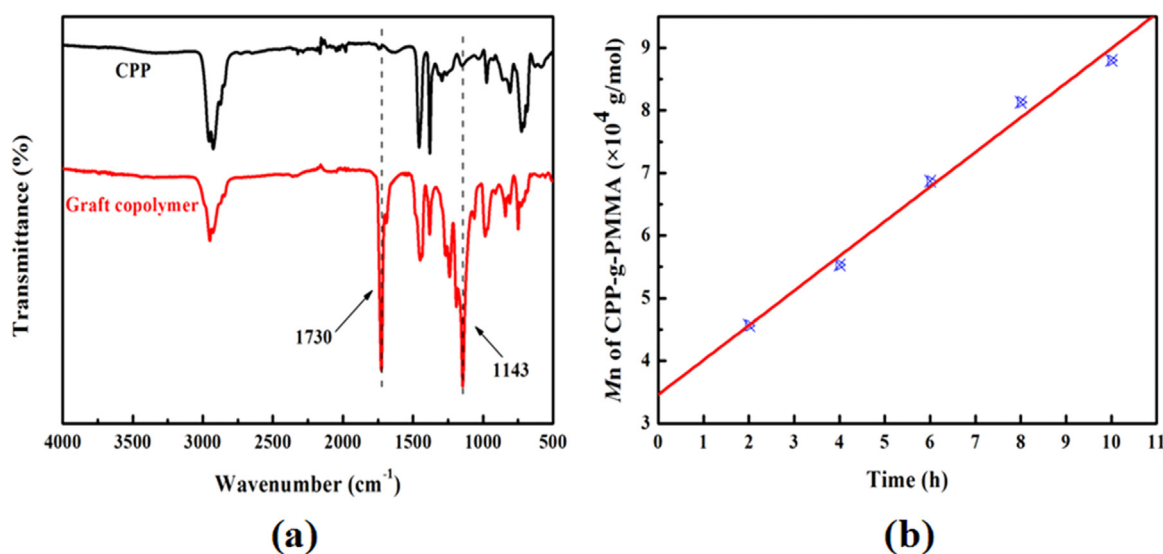
Fig. 1. (a) FTIR spectra of CPP and the graft copolymer; (b) Dependence of M_n on t.

Table 1
Polymerization of MMA initiated from CPP in NMP at 80 °C.

Code	Time (h)	[MMA]/[Cl]/[AlCl$_3$]/[FeCl$_2$]/[(PPh$_3$)$_2$] (molar ratio)	M_n	MWD
M0	0	–	35,000	–
M1	2	100/20/1/1/2	45,679	3.11
M2	4	100/20/1/1/2	55,346	3.01
M3	6	100/20/1/1/2	68,697	2.85
M4	8	100/20/1/1/2	81,330	2.80
M5	10	100/20/1/1/2	87,984	2.53
M6	6	100/20/0/1/2	33,471	6.49

added after the solution was bubbled by argon gas for 20 min. The system was sealed at 80 °C. When the designed polymerization time was over, the solution was cooled to ambient temperature and subsequently precipitated into ethanol. The precipitate was purified three times by redissolving in NMP and reprecipitating in ethanol. Finally, the product was filtrated, washed with ethanol and dried under vacuum at 45 °C until constant weight.

CPP-g-PMMA was characterized by FT-IR spectrometer (Thermo-Nicolet iS50, US). The number average molecular weight (M_n) and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC, Waters 1525, Waters). The degree of grafting (DOG) was calculated by the following Eq. [9]:

$$DOG(\%) = (M_n - M_{n0}) \times 100/M_{n0}$$

where M_{n0} and M_n are the number average molecular weight of the CPP and CPP-g-PMMA, respectively.

CPP-g-PMMA was dissolved in NMP. The weight ratio of CPP-g-PMMA/NMP was kept at 25/75. The solution was heated to 80 °C for 5 h and then deaerated under reduced pressure for 2 h, which was uniformly spread onto a clean glass plate by a casting bar. The glass plate was immediately immersed into 25 °C deionised water as a coagulation bath. The obtained membrane was washed with deionised water to remove the residual NMP. The final microporous membranes were vacuum freeze-dried for 10 h. The cross-sectional images of membranes were investigated using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi).

Membranes were activated in a electrolyte (LB315 type) for 24 h and assembled into the CR2430 coin-type cells in a dry
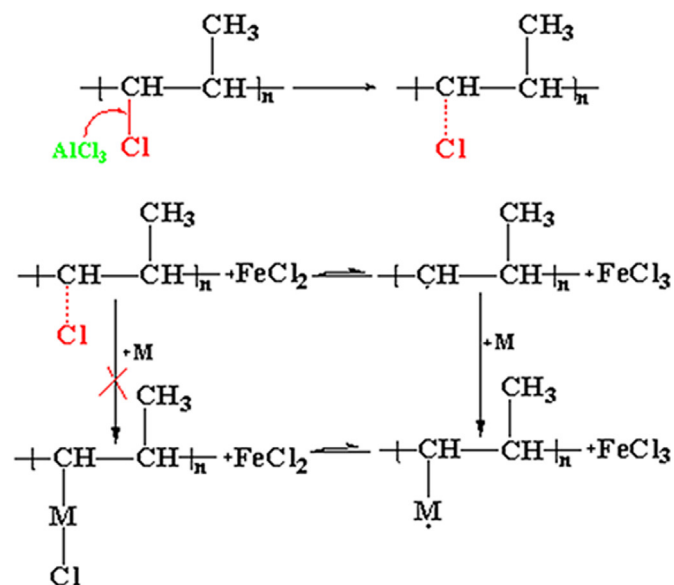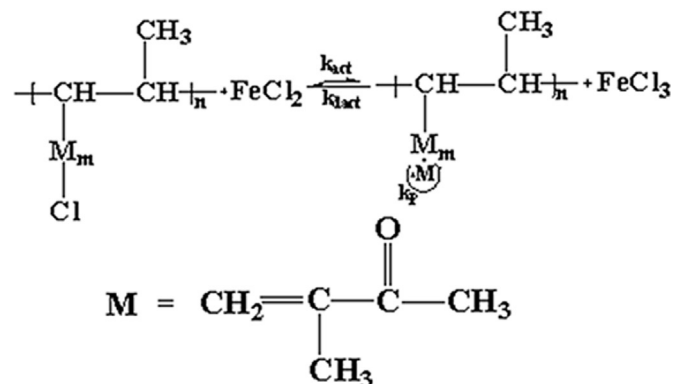

Fig. 2. The mechanism chart of ATRP.