

Notes

SYNTHESIS AND POLYMERIZATION OF TRI(2-PYRIDYL)METHYL METHACRYLATE

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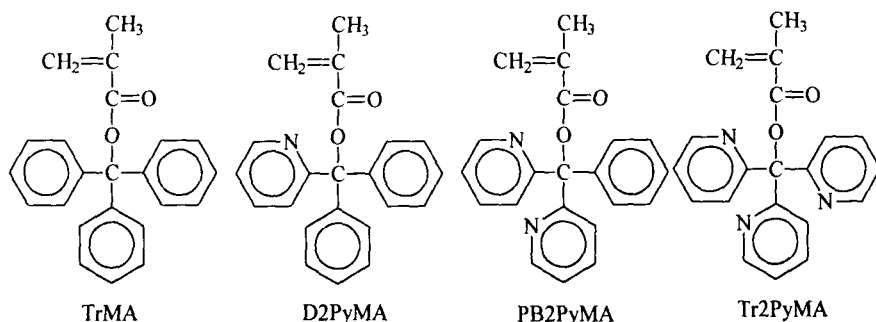
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Abstract A novel methacrylate monomer with bulky side group, *tri*(2-pyridyl)methyl methacrylate (Tr2PyMA), was synthesized and polymerized. The polymer obtained by radical polymerization exhibits high isotactic tacticity.

Keyword Optical activity, *Tri*(2-pyridyl)methyl methacrylate

INTRODUCTION

Various optically active polymers with chirality due mainly to the helical conformation have been attracting great attention^[1-3]. The helical chain polymer with optical activity has been successfully obtained from a chiral methacrylate monomers with bulky side group, for example, triphenylmethyl methacrylate (TrMA)^[4]. The optically active poly(TrMA) shows excellent chiral recognition ability when it is used as a chiral stationary phase for high performance ligand chromatography (HPLC)^[5] and the packed column has been widely used for separating optical isomers^[6]. However, this stationary phase has an inherent defect, its optical resolving power is gradually reduced by solvolysis of the ester group of the polymer with methanol which is the most useful eluent. Therefore, Okamoto *et al.*^[7] reported that the introduction of an electro-withdrawing 2-pyridyl group in place of one of the three phenyl groups of TrMA, i.e. diphenyl-2-pyridylmethyl methacrylate (D2PyMA), (Scheme 1) increases its resistance against the solvolysis of ester linkage by methanol^[8].



Scheme 1 Methacrylate monomers with bulky side groups

Afterwards, Ren *et al.*^[9] reported that phenyl[bis(2-pyridyl)]methyl methacrylate (PB2PyMA)

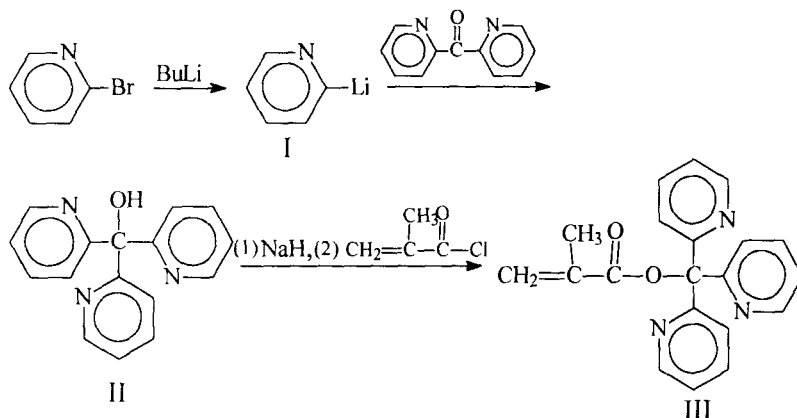
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(Scheme 1) which has two 2-pyridyl groups in the ester moiety can be regarded as a suitable monomer to form an optically active one-handed helix polymer which would be more durable to methanolysis than poly(TrMA) and poly(D2PyMA)^[10]. The present study aims to synthesize a novel methacrylate monomer, *tri*-(2-pyridyl)methyl methacrylate (Tr2PyMA) (Scheme 1), and to study its polymerization feature.

Experimental

Tr2PyMA was Synthesized as Follows



Preparation of 2-lithiopyridine (I)

Into a solution of *n*-butyllithium (0.1 mol) in 100 mL of ether cooled to -40°C (dry ice/methanol) under dry nitrogen, a solution of 2-bromopyridine (Aldrich) (16 g, 0.1 mol) in 40 mL of ether was added quickly from a dropping funnel with stirring to form 2-lithiopyridine (I). The obtained 2-lithiopyridine solution was stirred continuously for 20 min at -40°C and then cooled to -65°C for the following preparation.

Preparation of *tri*-(2-pyridyl) methanol (II)^[11]

A solution of di-2-pyridyl ketone (Aldrich) (18.4 g, 0.1 mol) in 60 mL of ether was added to the above solution of 2-lithiopyridine within a period of 30 min. The colour of the reaction mixture changed to dark blue. After the mixture was warmed slowly to room temperature, 100 mL of water and 50 mL of 1.0 mol sulfuric acid were slowly added in sequence, 13 g of crude product was obtained. The crude product was recrystallized from petroleum ether ($90\sim 120^\circ\text{C}$) several times to give yellow needle crystals of *tri*-(2-pyridyl) methanol (II) (11 g, yield 42.8%), m.p. $127\sim 128^\circ\text{C}$.

Elemental analysis of $\text{C}_{16}\text{H}_{13}\text{ON}_3$ (Calcd.): C 73.00%, H 4.94%, N 15.97%; (found): C 72.89, H 4.99%, N 15.83%. $^1\text{H-NMR}$ (250 MHz, in CDCl_3 , TMS) δ 8.52–8.56 (*m*, 3H, α -H in $(\text{C}_5\text{H}_5\text{N})_3$ —), 7.14–7.21 (*m*, 3H, β -H in $(\text{C}_5\text{H}_5\text{N})_3$ —), 7.61–7.71 (*m*, 3H, γ -H, 3H, ω -H in $(\text{C}_5\text{H}_5\text{N})_3$ —) and 7.70 (*s*, 1H, in —OH).

Preparation of *tri*-(2-pyridyl)methyl methacrylate (III)

Tri-(2-pyridyl) methanol (II) (7.9 g, 0.03 mol), NaH (1.5 g, 0.06 mol) and dried THF (100 mL) were added to a 250 mL flask and reacted at room temperature with stirring for 30 min, then heated to 50°C under nitrogen for another 3 h and left overnight at room temperature. Methacryloyl chloride (3.6 mL, 0.036 mol) was added drop-wise to the above suspended solution, stirred at room temperature for 1 h, heated to 50°C for 4–5 h, then left overnight at room temperature with stirring to obtain solid mixture. The solid mixture was separated out by filtration, washed with THF and ether several times. The filtrate was volatilized to crystallize out the crude product of *tri*-(2-pyridyl)methyl methacrylate. The crude product was recrystallized twice from benzene-hexane

(1/1, v/v) to give white crystals of tri(2-pyridyl)methyl methacrylate(Tr2PyMA)(III) (6.5g, yield 65%), m.p. 140–141 °C.

Elemental analysis of $C_{20}H_{17}O_2N_3$ (calcd.): C 72.51%, H 5.16%, N 12.69%; (found): C 72.48%, H 5.33%, N 12.53%. ^1H -NMR (250 MHz, in $CDCl_3$, TMS): δ 2.08 (s, 3H, in $-CH_3$), 5.70, 6.40 (m, 2H, in $=CH_2$), 8.51–8.55 (m, 3H, α -H in $(C_5H_5N)_3-$), 7.08–7.16 (m, 3H, β -H in $(C_5H_5N)_3-$), 7.60–7.70 (m, 3H, γ -H in $(C_5H_5N)_3-$) and 7.80–7.86 (m, 3H, ω -H in $(C_5H_5N)_3-$). MS m/e: 332(M^+ +1).

Polymerization of Tr2PYMA (III)

The polymerization procedure is the same as that reported in a previous paper^[9].

RESULT AND DISCUSSION

The results of polymerization of Tr2PyMA are shown in Table 1. In radical polymerization, low molecular weight (about 6,000) and optically inactive polymers were obtained. It is found that the lower polymerization temperature, i.e. polymerization by using more active initiator, would facilitate the polymerization to result in a higher yield. The bulky side group of tripyridylmethyl in Tr2PyMA monomer will induce the radical polymerization mechanism and the obtained polymer possesses higher isotactic tacticity (81%, by using BPPD initiator).

In all the anionic catalyst systems, the polymerization does not proceed completely. Okamoto *et al.*^[4] have synthesized several other triarylmethyl methacrylates with bulky side group and polymerized them via chiral anionic complexes. However, some monomers may be too bulky to form a high polymer and too long or too flexible to maintain a stable helical polymer chain. In addition, the selection of chirally anionic catalyst system would be very important for the polymerization of these monomers. For example, when the polymerization of D2PyMA with the complexes which were derived from (+)-tartaric acid and L-proline and polymerization of PB2PyMA by the complexes with (+)DDB, (-)DDB and (-)Sp(sparteine) ligands^[9] were carried out in toluene at $-78^\circ C$, the polymerization yield and specific rotation of the obtained polymers were obviously low as compared with that of one-handed helical poly(TrMA). Among the chiral ligands examined for the helix-sense-selective polymerization of D2PyMA so far, it is found that the most effective one is (+)PMP^[9, 10]. Therefore, the polymerization of D2PyMA and PB2PyMA was greatly influenced by chiral initiator system. The study of novel initiator for the polymerization of Tr2PyMA is under way.

Table 1. Polymerization of D2PyMA, B2PyMA, Tr2PyMA with several catalyst systems

Type	Cat.	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Yield (%)	$[\alpha]_{365}^{25}$	Tacticity(%) ^a			Ref.
							mm	mr	rr	
D2PyMA	(+)DDB ^b /FILi ^c	Toluene	-78	15	100	-157	95	4	1	[5]
	(+)PMP/DPEDA-Li ^d	Toluene	-78	3	100	+1666	--	--	--	[5]
B2PyMA	(+)DDB/DPEDA-Li	Toluene	-78	70	30	+7.0	59	35	6	[7]
	(+)PMP/DPEDA-Li	Toluene	-78	24	94	+1355	97	2	1	[7]
Tr2PyMA	(+)DDB/DPEDA-Li	Toluene	-78	24	--	--	--	--	--	
	(+)PMP/DPEDA-Li	Toluene	-78	24	--	--	--	--	--	
	AIBN	Toluene	60	48	40	--	--	--	--	
	LPO ^e	Toluene	50	48	60	--	--	--	--	
	BPPD ^f	Toluene	45	48	80	--	81	0	19	

a) Determined by ^1H -NMR of poly(MMA) derived from corresponding polymers, b) (+)DDB: (S,S)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino) butanes, c) FILi: 9-fluorenyllithium, d) (+)-PMP:(S)-(+)-(2-pyrrolidinylmethyl) pyrrolidine; DPEDA-Li: N, N'-diphenylethylenediamine monolithium amide, e) LPO: $(C_{11}H_{23}COO)_2$, BPPD: f) $(C_6H_5OCH_2CH_2-O-COO)_2$

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