SHORT COMMUNICATIONS

Stereospecific and Asymmetric Polymerization of Diphenylpyridylmethyl Methacrylates

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Extensive studies on the stereospecific polymerization of methacrylic acid esters have been carried out and the influence of the ester group on the tacticity has been studied in detail.¹ Among many esters, triphenylmethyl methacrylate (TrMA) is a unique monomer which forms a highly isotactic polymer in anionic polymerization with BuLi not only in toluene but also in THF, and even radical polymerization affords a polymer rich in isotacticity.^{2.3} Furthermore, an optically active poly-(TrMA) was obtained in the asymmetric polymerization with chiral anionic initiators^{4,5} and showed chirality due to helicity alone and was found useful for the preparation of a usable chiral packing material in the liquid chromatographic resolution of various racemic compounds.⁶⁻¹² In this communication, we report the stereospecific and asymmetric polymerization of diphenyl-2-pyridylmethyl methacrylate (D2PyMA) and diphenyl-4-pyridylmethyl metacrylate (D4PyMA) having structures similar to TrMA. The radical polymerization of these monomers, particularly that of D2PyMA gave highly isotactic polymers. The isotacticity of poly-(D2PyMA) may be highest among many polymers produced by a radical process. The optical activity of poly(D2PyMA) prepared by asymmetric polymerization changed slowly in solution.

D2PyMA was prepared from methacryloyl chloride and sodium diphenyl-2-pyridylmethoxide in THF and purified by recrystallization from hexane; mp 128—129°C. D4PyMA was prepared from silver



methacrylate and diphenyl-4-pyridylmethyl chloride in ether and recrystallized from ether; mp 101-102°C. Both monomers were identified by elemental analysis, IR, and NMR spectra. The polymerization was carried out in a glass ampoule under dry nitrogen. An initiator solution was added to a monomer solution in toluene. The reaction was terminated by adding a small amount of methanol and the reaction mixture was poured in a large amount of methanol. Poly(D2PyMA) was converted to poly(methacrylic acid) by refluxing in methanol containing hydrochloric acid overnight. Poly(D4PyMA) was not hydrolyzed under the above conditions but was so in concentrated sulfuric acid. These poly(methacrylic acid)s were methylated with diazomethane to give poly(methyl methacrylate)s (PMMAs).¹³ The molecular weight and tacticity of the polymers were estimated from the resulting PMMAs.

The results of the polymerization of D2PyMA are summarized in Table I. All the polymers were highly isotactic. The isotacticity of the polymer obtained with 2,2'-azobisisobutyronitrile (AIBN) may be

Initiator	[D2PyMA] [Initiator]	Temp °C	Time hr	Polymer						
				Yield	[α] ^{25 b} 365	DP	Tacticity/%			
							Ι	Н	S	
AIBN	100	60	24	36		95	86	11	3	
BuLi	20	-78	24	56		675	94	4	2	
Sp-BuLi	20	- 78	24	94	— 54°	398	94	4	2	
DDB-DPEDA-Li	20	- 78	4.5	99	$-307^{\circ c}$	62	91	5	4	
DDB-DPEDA-Li	30	78	24	100	-8°	108	93	4	3	
DDB-DPEDA-Li	50	- 78	24	100	$+145^{\circ}$	169	95	4	1	

Table I. Polymerization of D2PyMA in toluene^a

^a D2PyMA 1 g, toluene 20 ml.

^b In CHCl₃-TFE (9:1).

° $[\alpha]_{546}^{25} - 92^{\circ}$.

highest among many polymers produced by radical polymerization. The isotacticity of poly(TrMA) obtained under the same conditions was 64%.^{2,3} The higher isotacticity of poly(D2PyMA) is thus likely ascribable to the existence of a 2-pyridyl group. The lone pair electrons of this group may play an important role in the polymerization. Polymerization with BuLi gave a polymer of the highest degree of polymerization. This also seems to be due to the existence of the 2-pyridyl group. Only this polymer was insoluble in common organic solvents.

Polymerization by chiral anionic initiators, a (-)-sparteine (Sp)-butyllithium (BuLi) complex and a (2R, 3R)-(-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB)-N,N'-diphenylethylenediamine monolithium amide (DPEDA-Li) complex, afforded optically active polymers almost quantitatively. The chirality of the polymer must be due to a stable helical conformation prevailing in a one screw sense. This is a kind of



"atropisomerism" in which large ester groups are responsible for the existence of the enantiomeric structures of the polymer. The optical rota-

tion of the polymer depended greatly on polymerization conditions. The polymerization of D2PyMA with Sp-BuLi gave a (-)-polymer of a rather high degree of polymerization and the polymer soluble in a mixture of chloroform and 2,2,2-trifluoroethanol (TFE) (9:1) while the polymerization of TrMA under the same conditions yielded a polymer of large positive rotation.4.5 The optical rotation of poly(D2PyMA) changed from a large negative to a positive value as the molar ratio of the monomer to DDB-DPEDA-Li increased. The specific rotations of these polymers in chloroform-TFE (9:1) slowly changed to a positive direction with time. For instance, the rotation of a polymer ([α]_{365}^{25} -307°) in Table I became $+50^{\circ}$ after 5 days. This slow rotational change appears attributable to a conformational change.

Table II shows the results of the polymerization of D4PyMA. The triad isotacticity of the polymer prepared with AIBN was about 10% lower than that of poly(D2PyMA). Anionic polymerization with lithium compounds at -78° C gave highly isotactic polymers. The polymers obtained with Sp-BuLi showed opposite rotations in chloroform-TFE (90:10) and in dichloroacetic acid. Although the specific rotations of the polymers are low compared with those of poly(D2PyMA) and poly-(TrMA), the content of the prevailing helical structure seems to be comparable because the ellipticity of poly(D4PyMA) around 260 nm in the circular dichroism spectrum was similar to those of poly(D2PyMA) and poly(TrMA). The optical rotation of poly(D4PyMA) in chloroform-TFE

Asymmetric Polymn. of Methacrylates

Initiator	T		THF-soluble part		THF-insoluble part							
	°C	%	%	[α] ²⁵ (THF)	%	\overline{DP} -	$[\alpha]_{546}^{25}$		Tacticity/%			
							(b)	(c)	I	Н	S	
AIBN	60	15				47			76	19	5	
BuLi	- 78	53	6		47	55		_	90	5	5	
Sp–BuLi	0	85	9	$+5^{\circ}$	76	93	$+1^{\circ}$		68	20	12	
Sp-BuLi	-78	87	0		87 ^d	75	$+27^{\circ}$	-40°	94	3	3	
DDB-DPEDA-Li	- 78	78	3		75	45	—	$+14^{\circ}$	88	8	4	

Table II. Polymerization of D4PyMA in toluene for 24 h^a

^a D4PyMA 1 g, toluene 10 ml, [D4PyMA]/[Li] = 20.

^b CHCl₂COOH.

° CHCl₃-TFE (9:1).

^d $[\eta] = 0.19 \,\mathrm{dl}\,\mathrm{g}^{-1}$ (30°C, CHCl₂COOH).

slightly decreased with time but was much more stable than that of poly(D2PyMA).

Optically active poly(D2PyMA) and poly(D4-PyMA) showed different chiral discrimination ability for racemic compounds when used as packing materials in liquid chromatography. The poly-(D2PyMA) showed a higher capacity for chiral recognition when a polar eluent such as methanolwater was used while chiral recognition by poly(D4PyMA) was more pronounced when a nonpolar eluent was employed. This difference seems due to the difference in the extent to which hydrogen bond formation can occur. The details of the optical resolution will be published elsewhere.

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