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Helix-Sense-Selective Polymerization of N,N-Diphenyl (Meth)acrylamide by Anionic Catalysts

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Abstract: In this paper, the helix-sense-selective polymerization of N,N-diphenyl acrylamide (DPAA) and N,N-diphenyl methacrylamide(DPMAA) were studied with living helix prepolymer as anionic initiator, and the chiral optical properties of the obtained polymers were investigated too. It was shown that optically active polymers of DPAA and DPMAA could be obtained under the experimental condition, and exhibited the same screw sense as that of the prepolymer.

Keywords: Helix-sense-selective polymerization, N,N-diphenyl (meth)acrylamide, specific rotation.

Recently, extensive studies on optically active polymers with rigid single sense helix conformation have been made, since Okamoto's sophisticated work on poly(triphenylmethyl methacrylate(TrMA)) and analogues[1]. The interest for asymmetric polymerization is not only because it is an efficient way of preparation of optically active polymers but also because it provides an insight to the polymerization mechanism. In this communication, we describe a kind of helix-sense-selective polymerization of N,N-diphenyl acrylamide(DPAA) and N,N-diphenyl methacrylamide(DPMAA). TrMA, DPAA, DPMAA were prepared according to literatures[2,3]. The polymerization was finished by standard anionic polymerization techniques[4]. An H-pattern flask was used when copolymer was prepared. Dry toluene was added to the left part of the H-pattern flask where monomer A was placed. After the polymerization completed, some amount of dry THF was added to the left part, after some time the pressure in the right part of the flask was reduced, the solution of prepolymer was transferred partially to the right part of the flask where monomer B in THF was placed just before. The residue of prepolymer was terminated by addition of a small drop of methanol just after the transfer. The monomer B was polymerized by the initiation of the added living prepolymer. After a given period, the polymerization was terminated. The prepolymer and the block copolymer were taken out and precipitated in methanol and purified by redissolution and reprecipitation.

Y. Okamoto reported that poly(TrMA) can form rigid helix when the degree of polymerization(DP)>9[5]. However when THF was used as solvent , even in the mixture of

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toluene and THF in anionic asymmetric polymerization, the coordination between lithium and chiral ligand could be interfered by THF[6], therefore optically active polymer could not be obtained. In contrast to the poor polymerizability of DPMAA, DPAA gave optically active polymer by polymerization with optically active anionic initiator. The results were given in **Table 1**.

Table 1 The results of asymmetric homopolymerization of various monomers at -78°C[a]

No.	Monomer	Initiator[b]	Solvent	Time(hr)	Yield[c](%)	$[\alpha]_D^{20}$ [d]
1	TrMA	FlLi-((+)DDB)	Toluene	7.0	100	+340
2	TrMA	FlLi-((+)DDB)	Toluene/THF (5/1 V/V)	7.0	100	0
3	DPAA	FlLi-((-)Sp)	Toluene	3.0	100	-60
4	DPMAA	FlLi-((+)DDB)	Toluene	7.0	0	---
		FlLi-((-)Sp)	Toluene	7.0	0	---

a: [ligand]/[Li]=1.2(mol), [M]/[Li]=20(mol), [toluene]/[M]=20(v/w), No.3 was polymerized at -90 ℃. b: Complexes of 9-fluorenyllithium(FlLi) with (-)sparteine((-)Sp), (s,s)-(+)-2,3-dimeth-oxy-1,4-bis(dimethylamine) butane((+)DDB) as anionic initiators. c: CH_3OH insoluble part. d: Measured in THF, concentration, 0.4.

The obtained prepolymer could be seen as the first block of the two-block copolymer prepared in helix-sense-selective polymerization(**Table 2**). The gel permeation chromatography(GPC) of prepolymer and block copolymer were shown in **Figure 1**. Due to the presence of THF, monomer B could be asymmetrically polymerized without the action of chiral ligand, that meant the screw sense of the second block was controlled only by the prepolymer. From the results shown in **Table 2**, all the second blocks exhibited the same screw sense as that of the prepolymer since the signs of $[\alpha_2]_D^{20}$ were the same as that of $[\alpha_1]_D^{20}$. And **Figure 2** indicated that poly(DPAA) block had obvious

Table 2 Helix-sense-selective asymmetric polymerization by anionic catalysts[a]

No.	Prepolymer	Monomer(B)[b]	T(°C)	$\frac{W_A}{W_A+W_B}$	$[\alpha]_D^{20}$ [d]	$[\alpha_1]_D^{20}$ [d]	$[\alpha_2]_D^{20}$ [7]
1	TrMA	DPAA	-90	0.38[c]	+118	+101	+17
2	TrMA	DPMAA	-78	0.70[c]	+256	+172	+84

a: Initiator of prepolymer: FlLi-(+)DDB complex, [ligand]/[Li]=1.2(mol), [M]/[Li]=10(mol), [toluene]/[M]=20(v/w), temperature –78°C. b: Solvent: THF, [THF]/[M]=20(v/w), W_A/W_B=1/1(w/w). c: calculated from element analysis. d: Measured in THF, concentration, 0.4.

positive Cotton effect (The influence of poly(TrMA) segment has been eliminated by using the poly(TrMA) as background). This may be suggested that the propagation only along the original sense of prepolymer helix avoid repulsive steric interaction of the bulky side groups on adjacent residues. In addition, it is interesting that though DPMAA could not be homopolymerized under experimental conditions, the optically active block copolymer of poly(DPMAA) could still be obtained as shown in **Table 2**.

Figure 1 **GPC** curves of prepolymer and the block-copolymer **(No. 1** in **Table 2, ---** block copolymer**,**—prepolymer)

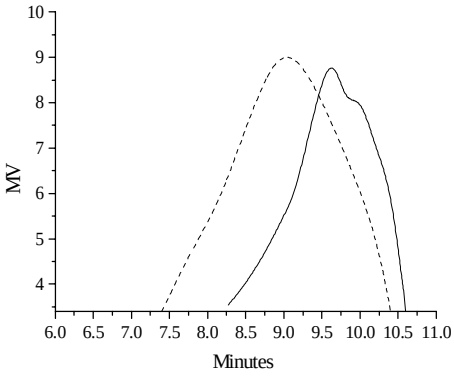
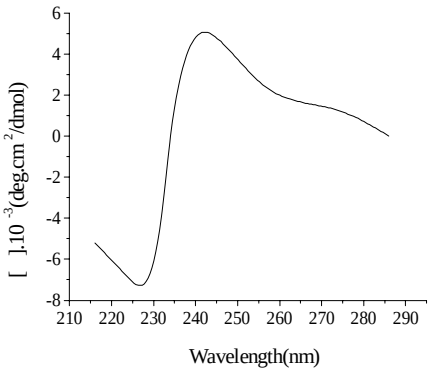


Figure 2 The **CD** spectrum of **Poly(DPAA)** block of **No. 1** in **Table 2**



From the results mentioned above, we can see that, DPAA and DPMAA could be helix-sense-selective polymerized when living helical prepolymer was used as anionic initiator and gave optically active polymers.

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7. For a helix homopolymer, every repeating unit in the polymer chain may contribute to optical rotation [α]. For a biblock copolymer the equation can be written as :

$$[\alpha] = \sum_{i=1}^{N_1} [\alpha_i] + \sum_{j=1}^{N_2} [\alpha_j] \qquad \text{or} \quad [\alpha] = [\alpha_1] + [\alpha_2] \qquad \left([\alpha_1] = \sum_{i}^{N1} [\alpha_i], \quad [\alpha_2] = \sum_{j}^{N2} [\alpha_j] \right)$$

where [α], [α_i]and [α_j] were the optical rotation of polymer and every repeating unit respectively , [α_1] and [α_2] were the apparent optical rotations of the two segments. If the specific rotation of prepolymer ([α_A]) in polymer was known, then [α_1]= $W_A/(W_A+W_B)$[α_A], W_A and W_B represented the weights of two segments in the copolymer respectively, so [α_2]=[α]-[α_1](The influence caused by structure dissymmetry in copolymer was neglected in the above discussion).

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