

“SERGEANTS AND SOLDIERS RULE” IN HELICAL SUBSTITUTED-ACETYLENE COPOLYMER EMULSIONS*

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Abstract The “sergeants and soldiers rule” occurring in helical copolymer emulsions derived from an achiral monomer (M1) and a chiral monomer (M2) was observed. TEM, GPC, and ¹H-NMR techniques in combination demonstrate the formation of nanoparticles constituted by the copolymers. CD and UV-Vis spectra show the (co)polymer chains in the nanoparticles adopt helical structures of a predominant helicity, and the copolymers follow the “sergeants and soldiers rule” in forming helical structure.

Keywords: Sergeants and soldiers rule; Helical polymer; Emulsion.

INTRODUCTION

Synthetic optically active polymers have gathered ever-increasing attention^[1, 2]. The optical activity may originate in configurational elements (chiral centers) and/or conformational elements (ordered secondary structures, *e.g.* helical conformations)^[3–6]. The polymers with helical conformations are specifically defined as helical polymers. Up to date, a number of artificially helical polymers have been reported in literature. Good examples include polyacrylates/polyacrylamides^[7, 8], polyisocyanates^[9, 10], polyisocyanides^[11, 12], polysilanes^[13], polyacetylenes^[14–16], polycarbodiimides^[17], polybinaphthyls^[18], vinyl polymers^[19–21], *etc.* Optically active helical polymers can be derived from chiral monomers or achiral monomers. In the latter group, external chiral factors are required to prepare chiral helical polymers, including asymmetric polymerization^[22, 23] with chiral catalyst (initiator, cocatalyst)^[24–26] or in asymmetric field^[27]; chiral induction with chiral additives is also an efficient approach^[28–30]. Additionally, introduction of a specific chiral monomer to an achiral monomer is also a remarkable route toward forming optically active helical polymers^[31], even though the homopolymer derived from the achiral monomer cannot form helices of preferable one-handed screw sense. Taking into the high cost of chiral monomers, copolymerization between an achiral monomer and a chiral comonomer should be a good choice for achieving optically active helical polymers. In the polymer systems constituted by chiral and achiral components, sergeants and soldiers rule^[32–35], namely the chiral amplification due to the achiral components “following” the helicity induced by the chiral components, is frequently observed. Nevertheless, such polymer systems reported so far are only limited to those obtained *via* solution polymerization^[31, 32]. In the present article, we will report the first observation of sergeants and soldiers rule in helical copolymer emulsions.

Taking into account the extensive practical applications of polymer emulsions derived from vinyl

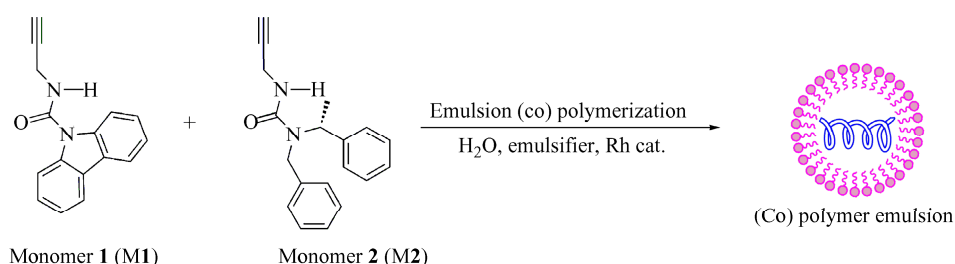
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monomers and the significant importance of emulsion polymerization in theoretical research, we have performed a series of emulsion polymerizations of acetylene-derived monomers^[36]. Such emulsion polymerizations have provided interesting optically active polymer emulsions (nanoparticles^[36] and hybrid nanoparticles^[37–39]). In particular interestingly, we developed a methodology for preparing optically active polymer nanoparticles from achiral monomers by using chiral micelles^[40, 41]. As an important extension of the previous studies, we in the present study explored emulsion copolymerizations of two monomers, *i.e.* an achiral monomer (M1) and a chiral monomer (M2), as structurally described in Scheme 1. The objective is to examine whether the copolymers and the emulsions thereof follow the sergeants and soldiers rule, as mentioned above. It is demonstrated that the helical copolymers such-obtained indeed obey this rule; more interestingly, optically active nanoparticles were directly obtained. The present study provides new insights into optically active helical (co)polymers and the emulsion copolymerization of chiral and achiral monomers.



Scheme 1 Monomer structure and emulsion copolymerization

EXPERIMENTAL

Materials

The solvents were distilled under reduced pressure under N_2 atmosphere in advance. Deionized water was used for emulsion polymerizations. Triton X-100 (polyethylene glycol *tert*-octylphenyl ether) was purchased from Aldrich and used as received without further purification. $(\text{nbd})\text{Rh}^+\text{B}^-(\text{C}_6\text{H}_5)_4$ (nbd = 2,5-norbornadiene) was prepared as reported^[42]. Monomers M1 and M2 were synthesized according to our earlier reports (M1, Ref. [43]; M2, Ref. [44]).

Characterization

^1H -NMR spectra were recorded on a Bruker AV600 spectrometer. Circular dichroism (CD) and UV-Vis spectroscopy measurements were conducted on a Jasco 810 spectropolarimeter. Before measurements, the polymer emulsions were diluted with deionized water. Monomer conversions were determined gravimetrically. Transmission electron microscopy (TEM) was performed with a HITACHI H-800 electron microscope on the polymer emulsions after a moderate dilution with deionized water. Emulsion particle size was determined based on TEM.

Emulsion (Co)polymerization

The typical emulsion polymerization procedure is stated as below, the details for which are depicted in our preceding article^[36]. A predetermined amount of Triton X-100 (1.37 g, 2.1 mmol) was dissolved in deionized water (15 mL) in a dry 50-mL glass flask equipped with a reflux condenser, a stirrer, an N_2 inlet and a dropping funnel. The Triton X-100 aqueous solution was stirred under 600 r/min at 30°C until the emulsifier was dissolved completely. The solution was then deoxygenated by purging with N_2 . After that, M1 (0.052 g, 0.21 mmol) dissolved in 2 mL DMF (*N,N*-dimethyl formamide) was dropwise added into the emulsifier aqueous solution. The solution mixture was stirred for another 20 min. $(\text{nbd})\text{Rh}^+\text{B}^-(\text{C}_6\text{H}_5)_4$ (0.002 g, 0.0042 mmol)/DMF (1 mL) solution was then dropwise added into the above monomer/emulsifier system and the monomer underwent polymerization under N_2 at 30°C for 3 h, providing polymer emulsions. To obtain pure polymer,

rotary evaporator was used to remove the water and DMF in the obtained emulsion, forming a mixture of emulsifier and polymer. Afterward, the product was added in water and stirred at room temperature for at least 5 min to make the emulsifier dissolve completely. Eventually, the solid residue was collected and concentrated to provide the pure polymer.

For emulsion copolymerizations, a similar emulsion polymerization process was taken with chiral and chiral co-monomers keeping constant in total concentration but with varied monomer ratio. The obtained (co)polymer emulsions were further subjected to CD and UV-Vis spectroscopy measurements. The pure (co)polymers were subjected to ¹H-NMR, GPC, CD and UV-Vis spectroscopy measurements.

RESULTS AND DISCUSSION

According to the effective emulsion polymerization methodology created by us earlier^[36], achiral monomer (M1) and chiral monomer (M2) were copolymerized in the presence of Triton X-100 as emulsifier and (nbd)Rh⁺B⁻(C₆H₅)₄ as catalyst in aqueous media. Emulsion (co)polymerizations proceeded quite smoothly. At the beginning of emulsion polymerization, the monomer/emulsifier aqueous systems were clear and nearly colorless. Soon after the addition of Rh catalyst, the polymerization systems became yellowish, as presented in Fig. 1. The yellow color is originated in the conjugated polymer backbones, as reported earlier^[36]. A difference in color is observed between the polymer emulsion from M1 (in this case, the polymer is denoted as polymer 1) and the copolymer emulsions (the copolymers are denoted as poly(1_x-co-2_y), *x* and *y*: the content of M1 and M2 in the copolymer, respectively), while the copolymer emulsions and the polymer emulsion from M2 (in this case, the polymer is denoted as polymer 2) are similar in color. The difference in (co)polymer emulsions color is caused by the UV-Vis absorption at varied wavelength, as discussed in more detail later.

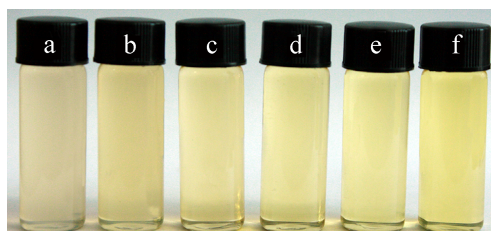


Fig. 1 Photographs of (co)polymer emulsions: (a) polymer 1; poly(1-co-2)s with M1/M2 of (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80 (mol/mol); and (f) polymer 2 (For more parameters, see Table 1.)

Table 1. Results of catalytic emulsion copolymerization^a

Entry	M1/M2 (mol/mol)	<i>M_n</i> ^b	<i>M_w</i> / <i>M_n</i> ^b	Diameter (nm) ^c	M1 in copolymer (mol%) ^d
Polymer 1	100/0	3300	1.15	83	n.d. ^e
Poly(1 _{0.8} -co-2 _{0.2})	80/20	3900	1.17	87	82
Poly(1 _{0.6} -co-2 _{0.4})	60/40	4200	1.28	80	61
Poly(1 _{0.4} -co-2 _{0.6})	40/60	5300	1.33	92	35
Poly(1 _{0.2} -co-2 _{0.8})	20/80	5500	1.47	86	22
Polymer 2	0/100	5900	1.63	75	n.d. ^e

^a Total monomer concentration, 1.1×10^{-2} mol/L; Rh cat. concentration, 2.3×10^{-4} mol/L; [Triton X-100]/[total monomer], 10/1 (mol/mol); Polymerization temp. 30°C, 3 h;

^b Determined by GPC (polystyrenes as standards, THF as eluent); ^c Based on TEM;

^d Determined according to ¹H-NMR; ^e Not determined

The obtained (co)polymer emulsions are observed with TEM after dilution with water. The TEM images are presented in Fig. 2. In all the examined six samples, nanoparticles were formed. The diameters of the nanoparticles were determined according to the TEM images, as shown in Table 1. All the particles are less than 100 nm in diameter (average diameter, 75–92 nm). Furthermore, with an increase of M2 content in the copolymers, the particles did not exhibit a pronounced change in size. The TEM images, together with the

measurements of GPC to be discussed next, definitely demonstrated the occurrence of emulsion polymerization and the formation of nanoparticles therein.

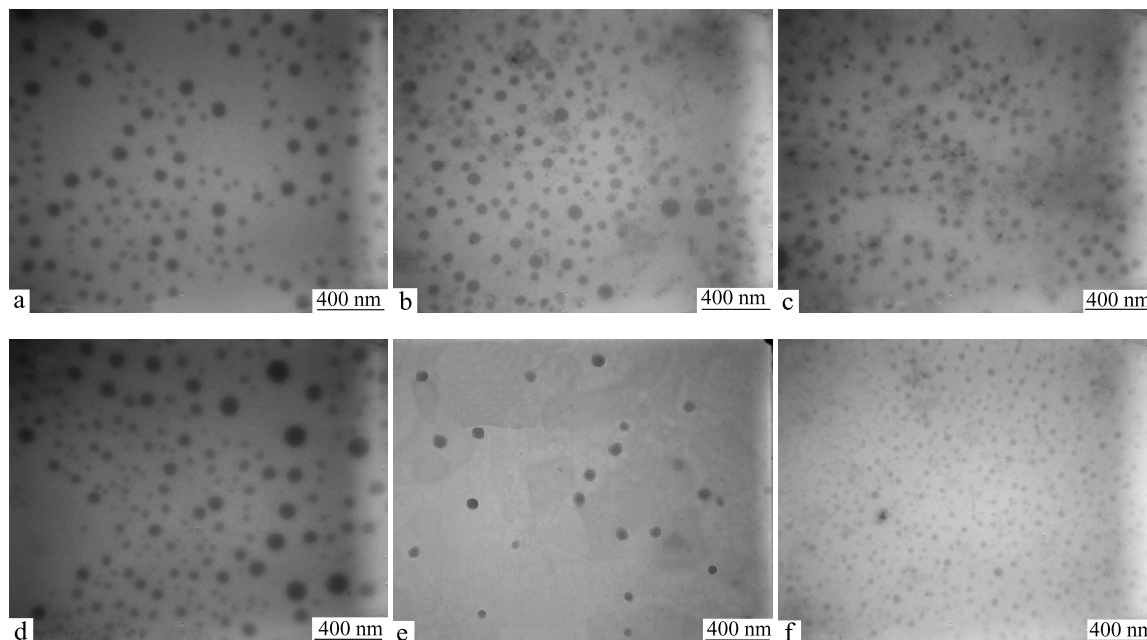


Fig. 2 TEM images of (co)polymer emulsions with different ratios of M1/M2: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80 and (f) 0/100 (mol/mol) (For more parameters, see Table 1.)

Even though we have performed a series of emulsion polymerizations of acetylene-derived monomers, the present study is the first one concerning emulsion copolymerizations of achiral monomer and chiral monomer. To understand the emulsion copolymerizations more clearly, we next examined the obtained (co)polymers in terms of polymer yield and number-average molecular weight (M_n) of the (co)polymers. The polymer yield for all the emulsion (co)polymerizations was nearly quantitative. Further, the pure (co)polymer after emulsion polymerization was obtained, as stated in the experimental section. The M_n and its dispersity for the (co)polymers are listed in Table 1.

We have investigated the copolymerization of M1 and M2 in THF solution, in which the obtained copolymers showed low to moderate M_n ^[43]. In the present study, the two comonomers underwent emulsion copolymerization smoothly, but the M_n 's of the copolymers are also not very high (3300–5900). This indicates that the relatively low M_n of the (co)polymers is predominantly dependent on the monomers' structure rather than the polymerization approach, *i.e.* emulsion polymerization versus solution polymerization. Moreover, the high yield of the copolymers (nearly 100%) enables us to consider that the compositions of the copolymers are the same as the corresponding monomer feed ratio. This assumption is further proved to be correct by the ¹H-NMR analysis of the copolymers. According to the method for determining the composition of substituted copolyacetylenes *via* ¹H-NMR technique^[45], we further calculated the copolymers composition and the results are also listed in Table 1. We included the ¹H-NMR spectrum of (**1**_{0.61}-*co*-**2**_{0.39}) as representative in Fig. 3. The data in Table 1 further facilitate us to conclude that the copolymers' composition is the same as the corresponding monomer feed ratio.

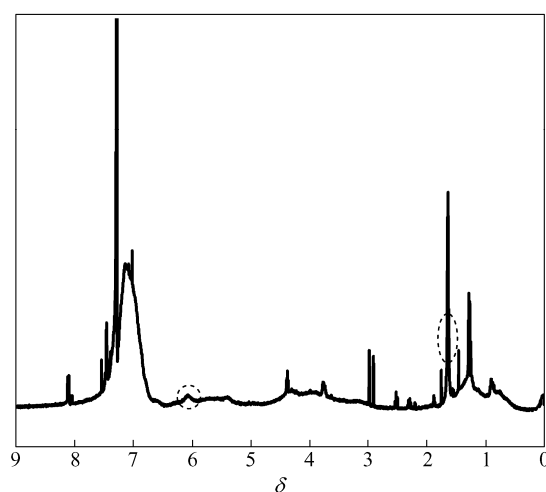


Fig. 3 ^1H -NMR spectrum of poly($1_{0.61}\text{-co-}2_{0.39}$) measured in CDCl_3 at 20°C

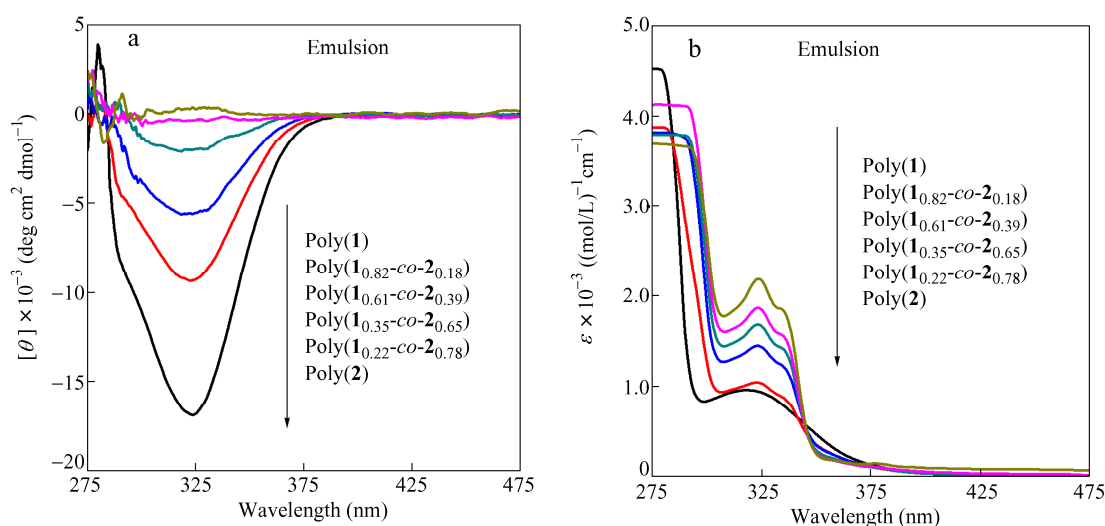


Fig. 4 (a) CD and (b) UV-Vis spectra of the copolymer emulsions with varied M1/M2 ratio. The concentration of polymers was *ca.* 0.1 mmol/L (determined by the monomer unit). The spectra were recorded at room temperature.

Our previous studies on the polymer emulsions derived from chiral substituted acetylenes show that such emulsions always exhibit optical activity, due to the formation of helical structures of predominant handed screw sense in the polymer backbones^[36–41]. This conclusion was made based on the measurements of CD and UV-Vis spectroscopy, which have been justified in their viability in analyzing the helical conformation of substituted polyacetylenes^[46]. The CD and UV spectra of the present polymer emulsions are presented in Fig. 4. For polymer **1**, no considerable CD signal was observed, due to the absence of chiral factors in this polymer^[43]. For polymer **2**, considerable CD effect was observed ($\lambda_{\text{max}} = 325 \text{ nm}$), just like the polymer obtained *via* solution polymerization, however, which showed the λ_{max} at 360 nm ^[44]. The difference in maximum wavelength will be mentioned again below. The intense CD signal of polymer **2** is originated from the formation of helical structures of predominant one handed screw sense^[44]. For the copolymers, considerable CD signal can be also observed around 325 nm . Furthermore, the CD signal intensity increased with increasing M2 content in the copolymers. This observation demonstrates that the present copolymers also follow the sergeants and soldiers rule, as observed in the copolymers obtained *via* solution copolymerization^[43]. Figure 4(b) shows the UV-Vis

absorptions of the copolymers. Nevertheless, since both the carbazole moiety in **M1** and the helical conformation of the copolymer backbones exhibited UV-Vis absorption around the wavelength (325 nm), it is difficult to draw definite conclusion from the UV-Vis absorption spectra.

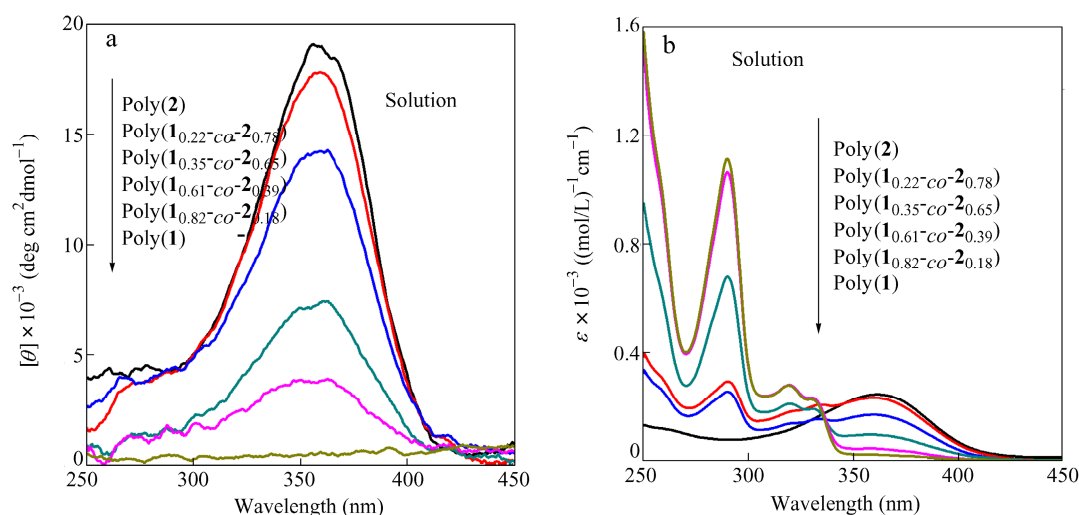


Fig. 5 (a) CD and (b) UV-Vis spectra of pure copolymer from the copolymer emulsion with varied M1/M2 ratio

The concentration of polymer was *ca.* 0.1 mmol/L (determined by the monomer unit). The spectra were recorded with CHCl_3 as solvent at room temperature.

We further measured the CD and UV-Vis spectra of the pure (co)polymers prepared *via* emulsion polymerization. The relevant spectra are illustrated in Fig. 5. When we compare the CD spectra of the copolymers, *i.e.* the poly(**1-co-2**) in the forms of emulsion vs. solution, we would find two remarkably interesting phenomena: (1) The CD spectra in Fig. 4(a) (emulsion) show CD signals with negative sign, while CD signals with positive sign are observed in Fig. 5(a) (solution). (2) The maximum wavelength appeared at approx. 325 and 360 nm in Figs. 4(a) and 5(a), respectively. A more clear comparison is made in Table 2, including the difference in CD and UV-Vis absorption between the polymer emulsions and the corresponding polymer solutions.

Table 2. A comparison between (co)polymer emulsions and solutions^a

	Emulsion ($\lambda_{\text{max}} = 325 \text{ nm}$)		Solution ($\lambda_{\text{max}} = 360 \text{ nm}$)	
	$[\theta] \times 10^{-3} \text{ (deg cm}^2 \text{ dmol}^{-1}\text{)}$	Abs	$[\theta] \times 10^{-3} \text{ (deg cm}^2 \text{ dmol}^{-1}\text{)}$	Abs
Polymer 1	0	2.17	1.62	0.02
Poly(1 _{0.8} -co- 2 _{0.2})	−0.55	1.84	3.84	0.04
Poly(1 _{0.6} -co- 2 _{0.4})	−2.24	1.66	7.39	0.09
Poly(1 _{0.4} -co- 2 _{0.6})	−5.59	1.43	14.23	0.17
Poly(1 _{0.2} -co- 2 _{0.8})	−9.46	1.02	17.82	0.23
polymer 2	−16.86	0.93	19.02	0.24

^a The data in this table are collected based on Figs. 4 and 5.

Regarding the opposite CD signal signs mentioned above (Fig. 4a versus Fig. 5a), we have observed a same phenomenon in our earlier study dealing with chiral helical polymer **2**^[47]. The detailed driving force for this phenomenon is still not clear yet. Nevertheless, it seems that the formation of nanoparticles in the course of emulsion polymerization forced the polymer chains to adopt an opposite helical screw sense against that in the solution state. For the different maximum CD wavelengths observed in Fig. 4(a) versus Fig. 5(a), we also ever observed this phenomenon in other polymer emulsions derived from substituted acetylenes^[47]. The blue shift in CD spectra in the form of polymer emulsion is due to the closely packing of the polymer chains in the

nanoparticles^[48].

From the CD and UV-Vis spectra in Fig. 5 and the data in Table 2, We find that the helical screw sense of the copolymers is decided by the chiral monomer units. Accordingly, we can reasonably conclude that the copolymers follow the sergeants and soldiers rule, even they were prepared *via* emulsion polymerization.

CONCLUSIONS

Achiral **M1** and chiral **M2** underwent emulsion copolymerizations in aqueous media. The copolymerizations proceeded smoothly, providing the corresponding copolymers with the same composition as the corresponding monomer feed ratio. The CD spectra demonstrate the optical activity of the (co)polymer emulsions consisting of chiral monomer units. More importantly, the copolymers as-prepared *via* emulsion polymerization obey the sergeants and soldiers rule, as observed earlier in the corresponding copolymers prepared *via* solution copolymerization. This study enables us to acquire deeper understanding of the optically active helical copolymers derived from chiral/achiral comonomers.

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