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Alternating Copolymerization of Propylene Oxide and Carbon Monoxide to form Aliphatic Polyesters

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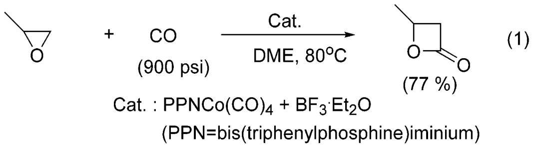
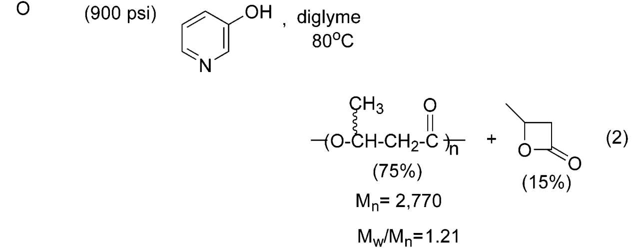
ABSTRACT: A new catalyst system for the alternating copolymerization of propylene oxide and carbon monoxide to form aliphatic polyesters is developed. The reaction of propylene oxide and carbon monoxide using $Co_2(CO)_8$/**A**(6,7-dihydro-5,8-dimethyldibenzo[*b,j*]-1,10-phenanthroline)/$PhCH_2Br$ as a catalyst, afforded atactic PHB in high molecular weight ($M_n = 19\,400$, $M_w/M_n = 1.63$) and 55% yield at 80 °C under 900 psi of carbon monoxide in benzene.

The metal-catalyzed carbonylation of epoxides such as ethylene oxide or propylene oxide to the corresponding β-lactones[1] or β-hydroxy esters (carbonylation with alcohol)[2] has been known for a long time. An effective catalyst is $Co_2(CO)_8$, and usually the reaction requires high pressures (200−300 atm) and high temperatures (up to 150 °C). In many cases involving the carbonylation of epoxides to β-lactones, polyester oligomers were obtained as the major product along with small amounts of β-lactones, and it was considered that the polyester oligomer can result from the β-lactone formed during the reaction.

Recently we developed a new catalyst system (PPN-$Co(CO)_4 + BF_3Et_2O$) (PPN = bis(triphenylphosphine)-iminium) which produces β-lactones selectively by the carbonylation of epoxides (eq 1).[3]



In this research, we demonstrated that polyesters can be obtained by the direct copolymerization of epoxides and carbon monoxide using different catalyst systems. This finding was also reported by another research group using an IR online monitoring method.[4] For example, the $Co_2(CO)_8$ and 3-hydroxypyridine catalyst system, claimed by Drent and co-workers[1i] to form β-lactones from epoxides in high yields, in fact afforded 75% of atactic poly(β-hydroxybutyrate) (PHB) oligomer ($M_n = 2770$, $M_w/M_n = 1.21$) and 15% of β-butyrolactone from the carbonylation of propylene oxide (eq 2).



When we reacted β-butyrolactone or a mixture of β-butyrolactone and propylene oxide under exactly the same reaction conditions, β-butyrolactone was recovered in almost quantitative yield. In this catalyst system, $HCo(CO)_4$ can be formed as an active catalytic species from $Co_2(CO)_8$ and 3-hydroxypyridine,[5] and the nucleophilic attack of deprotonated 3-hydroxypyridine anion on the less hindered carbon atom of the propylene oxide may assist the ring opening of propylene oxide.[4,6]

From these results, we can anticipate that the selective synthesis of β-lactones or polyesters, by the carbonylation of epoxides, primarily depends on the nature of the ring opening of the epoxides (Scheme 1). Ring opening of the heterocycle assisted by a Lewis acid or $HCo(CO)_4$, and backside attack of $^{-}Co(CO)_4$ on the less hindered carbon, can give intermediates I or III (Scheme 1). After CO insertion, ring closure of intermediate II can produce the β-lactone. In the case of intermediate IV, it seems likely that another epoxide insertion into the acyl carbon−cobalt bond is favored rather than ring closure. If a base such as pyridine is present in the reaction mixture, it can form $[(py)Co(CO)_3]^+[Co(CO)_4]^-$ with $Co_2(CO)_8$,[5] and $[(py)Co(CO)_3]^+$ species promoting the ring opening of the epoxide can accelerate the formation of polyesters.

Poly(β-hydroxybutyrate) (PHB) is a naturally occurring, biodegradable[7] and biocompatible[8] thermoplastic and considered as a class of potentially important biopolymers in industry. In an effort to produce higher molecular weight PHB, most studies have focused on the metal-catalyzed ring-opening polymerization (ROP) of β-butyrolactone.[9−14] Among these studies, ROP effected using diiminate zinc complexes as catalysts provided more than 100 000 g/mol of number-average molecular weights (M_n) with high polymer yields.[14]

Given these findings, the alternating copolymerization of propylene oxide and carbon monoxide should be a more efficient synthetic route for PHB. We reasoned that the development of a new catalyst system which can produce polymers in higher molecular weight and higher yields would be a noteworthy advance in this field.

In the beginning, the investigation was based on the $Co_2(CO)_8$ and 3-hydroxypyridine catalyst system which copolymerizes propylene oxide and carbon monoxide.[3,4] First we tested the possibility of using pyridine and *p*-toluenesulfonic acid (*p*-TsOH) as a proton source

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Scheme 1

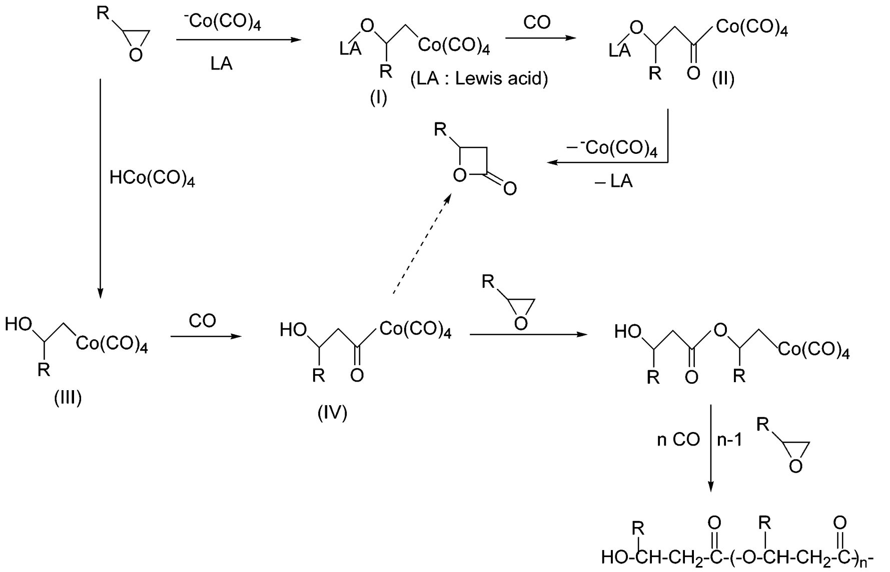
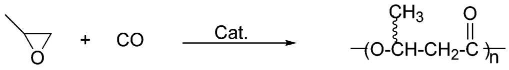


Table 1. Copolymerization of Propylene Oxide and CO[a]

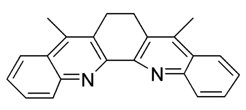


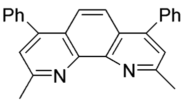
entry	cat. (molar ratio)	solvent	polymer yield(%)[b]	M_n ($\times 10^{-3}$)[c]	M_w/M_n[c]
1	$Co_2(CO)_8$ + pyridine + *p*-TsOH (1/2/2)	THF	36	3.1	1.23
2	$Co_2(CO)_8$ + 2,2′-bipyridine + *p*-TsOH (1/2/2)	THF	37	5.1	1.31
3	$Co_2(CO)_8$ + 2,2′-bipyridine + *p*-TsOH (1/2/1)	THF	41	4.7	1.28
4	$Co_2(CO)_8$ + 2,2′-bipyridine + *p*-TsOH (1/1/1))	THF	59	4.8	1.31
5	$Co_2(CO)_8$ + 2,2′-bipyridine + *p*-TsOH (1/1/1)	benzene	65	6.7	1.55
6	$Co_2(CO)_8$ + 2,2′-bipyridine + *p*-TsOH (1/1/1)	CH_2Cl_2	37	4.4	1.38
7	$Co_2(CO)_8$ + 1,10-phenanthroline + *p*-TsOH (1/1/1)	benzene	43	9.5	1.39
8	$Co_2(CO)_8$ + 1,10-phenanthroline + CH_3I (1/1/1)	benzene	50	9.3	1.47
9	$Co_2(CO)_8$ + 1,10-phenanthroline + $PhCH_2Br$ (1/1/1)	benzene	54	9.7	1.41
10	$Co_2(CO)_8$ + **A** + $PhCH_2Br$ (1/1/1)	benzene	55	19.4	1.63
11	$Co_2(CO)_8$ + **B** + $PhCH_2Br$ (1/1/1)	benzene	50	12.3	1.41

[a] Reaction conditions (entry 10): 1 mL of propylene oxide, 0.05 mmol (0.35 mol %) of $Co_2(CO)_8$, 0.05 mmol of **A**, and 0.05 mmol of $PhCH_2Br$ in 2 mL of benzene at 80 °C under 900 psi of CO for 20 h. [b] Isolated yield after purification with an ether/*n*-hexane (1/1) mixture. [c] Determined by GPC calibrated with polystyrene standards in THF.

instead of 3-hydroxypyridine. Use of $Co_2(CO)_8$/pyridine/*p*-TsOH as the catalyst system for the copolymerization of propylene oxide and carbon monoxide at 80 °C under 900 psi of CO for 20 h in THF gave PHB in similar molecular weight and polydispersity ($M_n = 3100$, $M_w/M_n = 1.23$), but in lower yield compared to $Co_2(CO)_8$ and 3-hydroxypyridine (eq 2 and Table 1, entry 1). When 2,2′-bipyridine was used instead of pyridine, the M_n increased to 5100 from 3100 (Table 1, entry 2).

The role of pyridine-derived compounds could be similar to that of 3-hydroxypyridine. We then examined different molar ratios of $Co_2(CO)_8$/2,2′-bipyridine/*p*-TsOH under the same reaction conditions and found that a 1/1/1 molar ratio gave the highest yield of the polymer, but the molecular weight was similar for other ratios (Table 1, entries 2−4). Among the solvents, benzene afforded higher molecular weights and higher polymer yields compared to THF or CH_2Cl_2 (Table 1, entries 4−6). The molecular weights of PHB (entries 1−6 of Table 1) were lower than the theoretical M_n (based on mol % catalyst), which should be about 14 500. One possible reason for this behavior may be the presence of traces of water in the reaction mixture. The same reaction as that of entry 5 (Table 1) in the presence of 3A molecular sieve gave an almost identical result. To change the active catalyst species from $HCo(CO)_4$ to $RCOCo(CO)_4$, we prepared, in situ, $PhCH_2COCo(CO)_4$[15] and $CH_3COCo(CO)_4$ as active catalytic species by the reaction of benzyl bromide and iodomethane, respectively, with $Co_2(CO)_8$ and CO under the reaction conditions. Recently, the intermediates of the cobalt carbonyl catalyzed carbonylation of benzylic halides were definitively identified.[16] Benzyl bromide gave a higher polymer yield compared to iodomethane, but the molecular weight was not changed (Table 1, entries 7−9). Finally, we tested bulkier and more basic diimines relative to 2,2′-bipyridine, such as 1,10-phenanthroline, 6,7-dihydro-5,8-dimethyldibenzo[*b*,*j*]-1,10-phenanthroline (**A**) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (**B**). When **A** was used with $Co_2(CO)_8$ (0.35 mol %) and benzyl bromide in benzene, PHB was formed in higher molecular weight ($M_n = 19\,400$, $M_w/M_n = 1.63$) and 55% yield of the polymer (Table 1, entry 10). To confirm that PHB is formed either by direct copolymerization of propylene


(**A**)



(**B**)

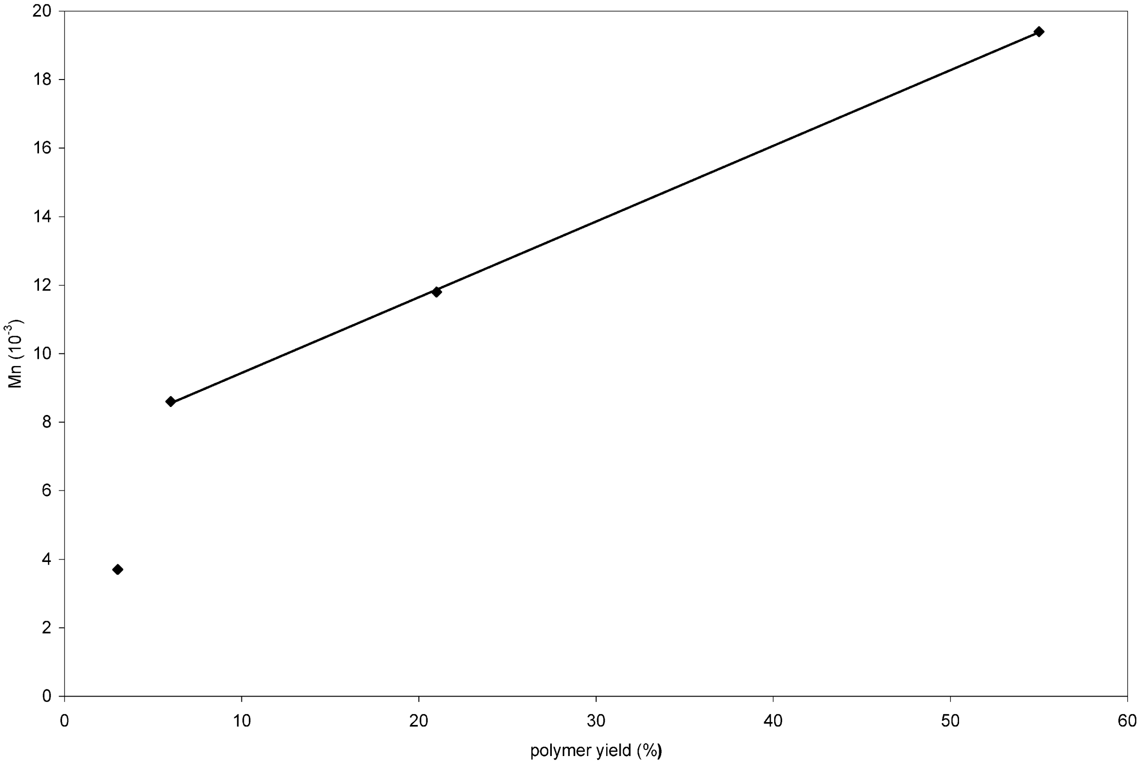


Figure 1. Relationship between polymer yield and M_n in the copolymerization of propylene oxide and CO under the conditions of entry 10, Table 1.

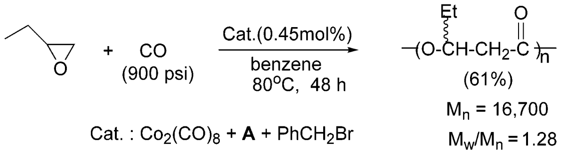
Table 2. Molecular Weights and Polydispersities of PHB Obtained under the Conditions of Entry 10, Table 1

polymerization time (h)	polymer yield (%)	M_n ($\times 10^{-3}$)	M_w/M_n
5	3	3.7	1.08
10	6	8.6	1.21
15	21	11.8	1.27
20	55	19.4	1.63

oxide with CO or by ring-opening polymerization of β-butyrolactone (which can be generated during the reaction) under the newly developed catalyst system, we attempted the reaction using β-butyrolactone instead of propylene oxide under the reaction conditions of entry 10, Table 1. No PHB was obtained, and β-butyrolactone was recovered. Although this copolymerization was not completed under the reaction conditions, narrow polydispersities were obtained in all cases (Table 1, entries 1−11). To confirm the potential pseudo-living behavior of this copolymerization, we measured molecular weights and polydispersities at the different polymers (Table 2, Figure 1). Indeed, the number-average molecular weight (M_n) increases linearly with increase of the polymer yield (from 6% to 55%) (Figure 1).

The ^{13}C and ^{1}H NMR spectra of polymeric PHB reveal regioregular, perfect alternating and atactic structure[9] (Figures 2 and 3).

As far as we are aware, this is the first successful copolymerization of propylene oxide and carbon monoxide. (Until now only oligomeric or very low molecular weight PHB was obtained by the copolymerization of propylene oxide and carbon monoxide.[1,3,4]) Application of the catalyst system to the copolymerization of 1,2-epoxybutane and carbon monoxide was also successful and afforded atactic poly(β-hydroxyvalerate) (PHV)[17] in high molecular weight (M_n = 16 700, M_w/M_n = 1.28) and in 61% yield (eq 3).



(3)

In conclusion, we have developed a new catalyst system for the copolymerization of propylene oxide and carbon monoxide which can produce higher molecular weight PHB in comparison with other catalysts. Additional experiments are directed to controlling the stereochemistry of the copolymerization.

Experimental Section

General. All chemicals were purchased from Sigma-Aldrich Chemical Co. and were used as received. Propylene oxide and butylene oxide were distilled under reduced pressure using liquid nitrogen trap and stored over 3A molecular sieves under nitrogen. Dicobalt octacarbonyl was purchased from Strem Chemicals Inc. Solvents were dried and distilled under nitrogen before use. All NMR spectra were recorded in $CDCl_3$ on a Varian XL-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz). GPC analyses were carried out with a Waters instrument equipped with UV486 and 410 differential refractive index detectors and three Waters Styragel columns (columns were eluted with THF at 40 °C at 1 mL/min). All manipulations were performed under dry nitrogen.

General Polymerization Procedure. To a benzene (2 mL, freshly distilled) solution of $Co_2(CO)_8$ (0.05 mmol, 17 mg) in a glass liner containing a magnetic stirrer bar, 6,7-dihydro-5,8-dimethyldibenzo[*b,j*]-1,10-phenanthroline (**A**) (0.05 mmol, 15.5 mg), benzyl bromide (0.05 mmol, 9 mg), and 1 mL of propylene oxide were added, and the mixture was stirred for 10 min under N_2 at room temperature. The glass liner was transferred into a 45 mL of stainless steel autoclave, flushed three times with carbon monoxide, then pressurized to 900 psi, and placed in an oil bath (80 °C). After stirring for 20 h, the autoclave

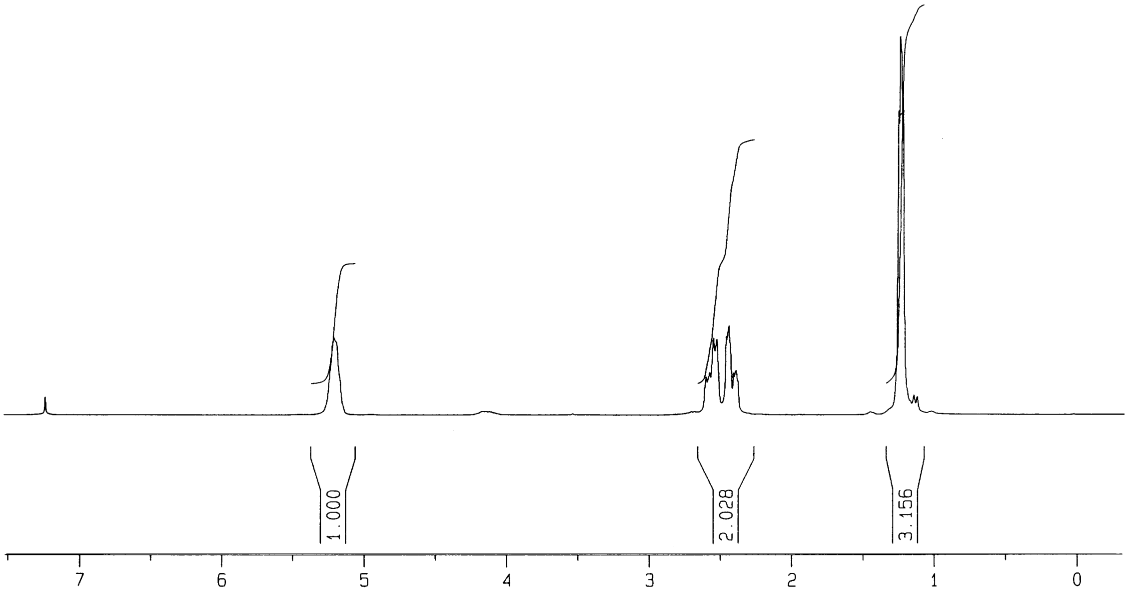


Figure 2. ^{1}H NMR spectrum of PHB produced by the copolymerization of propylene oxide and CO (entry 10, Table 1).

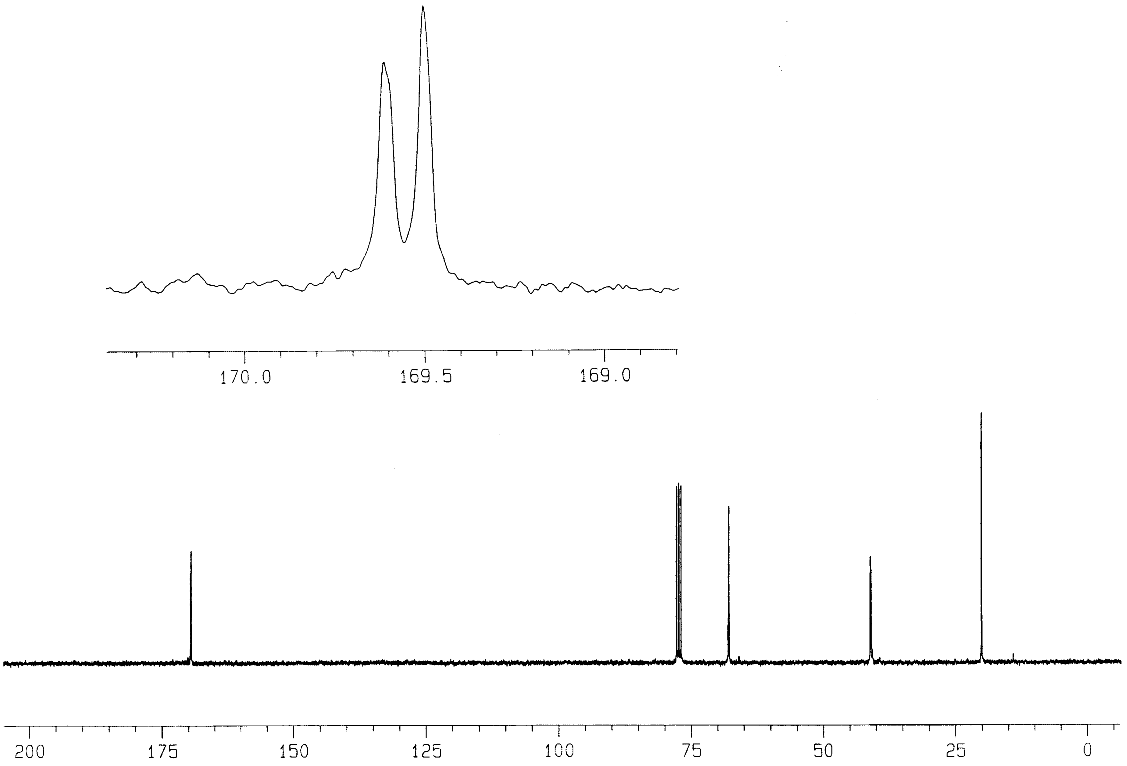


Figure 3. ^{13}C NMR spectrum of PHB produced by the copolymerization of propylene oxide and CO (entry 10, Table 1).

was cooled and excess gas was released. The reaction mixture was diluted with 15 mL of chloroform and transferred to another flask, 3−4 drops of concentrated HCl was added, and the mixture was stirred for 30 min in air at room temperature. The solution was dried with anhydrous $MgSO_4$ and filtered; rotary evaporation of the filtrate gave the crude polymer. The latter was extracted with a mixture of 30 mL of ether and *n*-hexane (1/1 volume ratio) for 2 h at room temperature and then dried overnight under high vacuum, giving 0.64 g of a colorless, highly viscous, paste-type polymer.

To confirm the possibility of fractionation of the polymer during the workup, we determined the molecular weights of the crude polymer (obtained by removing the solvent in vacuo followed by filtration of the diluted reaction mixture over a Celite/glass wool plug) and the purified polymer. There were only small differences of molecular weights obtained between the crude and purified polymers.

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