Preparation of Poly(methylene) by Dehalogenation Polycondensation of α,ω-Dibromoalkanes and Properties of the Polymer

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ABSTRACT: A novel route to yield linear poly(methylene) from α,ω-dibromoalkanes has been developed by utilizing a copper-catalyzed C–C coupling reaction between alkyl dibromide and a Grignard reagent. Copper compounds catalyze the dehalogenation polycondensation of α,ω-dibromoalkanes, $Br-(CH_2)_n-Br$ (n = 5, 6, 8, 10, 12), with Mg via Grignard reagent to give linear poly(methylene) having molecular weight in the range 2000–3700 ($nBr-(CH_2)_m-Br + nMg$ [+Cu] $\rightarrow -(CH_2)_{mn}- + nMgBr_2$). $CuBr(PPh_3)$ has the highest catalytic activity among the copper compounds tested. IR and NMR spectroscopy indicates that the polymer has a linear structure with CH_3 and CH_2Br terminal groups. The IR data as well as the X-ray diffraction pattern, heat of fusion, and density of the polymer show that the poly(methylene) has a high degree of crystallinity. The GPC curve of the polymer roughly coincides with the most probable distribution curve of the molecular weight of the polymer. The copper-catalyzed dehalogenation polycondensation is also applied to preparation of thermally stable poly(*trans*-1,4-cyclohexylene)(ethylene) from *trans*-1,4-bis(bromomethyl)cyclohexane.

Introduction

It is known that treatment of haloalkanes with metals such as Na and K leads to C–C coupling of the haloalkanes[1]

$$2R-X + \text{metal} \rightarrow R-R \qquad (1)$$
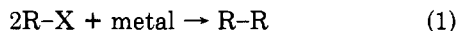
One may expect that application of this C–C coupling reaction to α,ω-dihaloalkanes affords poly(methylene)

$$nX-(CH_2)_m-X + \text{metal} \rightarrow -(CH_2)_{mn}- \qquad (2)$$
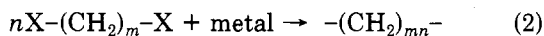
However, this type of dehalogenation polycondensation has not been realized by conventional methods using alkali metals, since the C–C coupling reaction does not proceed cleanly, presumably due to a radical nature of the active reaction intermediate in reaction 1.

In contrast to the conventional C–C coupling reaction and its low selectivity, a recently developed transition-metal-catalyzed C–C coupling reaction between a Grignard reagent, RMgX, and an organic halide, RX, proceeds with a high selectivity to give R–R in high yield[2]

$$RMgX + RX \xrightarrow{\text{[M]}} R-R + MgX_2 \qquad (3)$$

The C–C coupling reaction proceeds with such a high selectivity that application of this C–C coupling reaction to dihalo organic compounds is expected to give polycondensation products according to the following reaction route:

$$nX-R-X + nMg \rightarrow [nX-R-MgX] \xrightarrow{\text{[M]}} -(R)_n- + nMgX_2 \qquad (4)$$
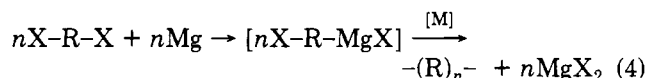
Previously, we reported that this type of dehalogenation polycondensation could be applied to dihalo aromatic compounds, and the polycondensation afforded thermostable and electric conducting aromatic polymers.[3] We now report on application of the polycondensation expressed by eq 4 to α,ω-dibromoalkanes, which are expected to give linear poly(methylene) on dehalogenation polycondensation

$$nBr-(CH_2)_m-Br + nMg \rightarrow [nBr-(CH_2)_m-MgBr] \xrightarrow{\text{[Cu]}} -(CH_2)_{mn}- + nMgBr_2 \qquad (5)$$
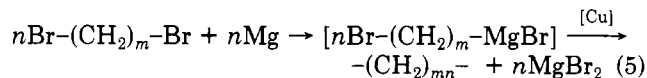
The objectives of the present study are twofold. First, preparation of poly(methylene) by dehalogenation polycondensation of α,ω-dihaloalkanes has no precedent, and comparison of the polymer prepared by the present method with poly(methylene) or poly(ethylene) by conventional methods is of considerable interest. Poly(ethylene) prepared by low-pressure coordination polymerization processes generally contains less branches than poly(ethylene) prepared by high-pressure radical processes.[4] The polymers prepared by the present method are expected to have less branches along the polymer chain if the polymerization proceeds by a nonradical mechanism. Second, we expected to gain information on the common mechanisms of the dehalogenation polycondensation

Table I
Copper-Catalyzed Dehalogenative Polycondensation of α,ω-Dibromoalkanes[a]

expt	monomer Br-$(CH_2)_n$-Br	catalyst[b]	temp, °C	time, h	yield,[c] %	mp, °C	M_v[d]
1	$n = 4$	$CuBr(PPh_3)$ (10)	-20	18	0		
2	$n = 5$	$CuBr(PPh_3)$ (10)	-20	18	18	115	
3	$n = 6$	none	room temp	12	0		
4	$n = 6$	$CuBr(PPh_3)$ (10)	room temp	12	80	125	3400
5	$n = 6$	CuBr (10)	room temp	12	40	114	
6	$n = 6$	$CuBr_2$ (17)	room temp	12	81	115	
7	$n = 6$	CuCl (5)	room temp	12	84	110	
8	$n = 6$	$CuBr(PPh_3)_3$ (10)	room temp	15	50	114	
9	$n = 6$	$AgNO_3$ (10)	room temp	12	15	85	
10	$n = 6$	$NiCl_2(bpy)$ (7)	room temp	12	0		
11	$n = 8$	$CuBr(PPh_3)$ (10)	room temp	12	80	124	2900
12	$n = 10$	$CuBr(PPh_3)$ (10)	room temp	12	85	120	
13	$n = 12$	$CuBr(PPh_3)$ (10)	room temp	14	86	126	3700

[a] In tetrahydrofuran. [monomer] = 0.5-1.5 M. [b] PPh_3 = triphenylphosphine; bpy = 2,2'-bipyridine. (mmol of catalyst)/(mol of monomer) is given in parentheses. [c] Yield is based on carbon recovered, which was calculated from the weight and carbon content of the polymer (yield = (weight of carbon in polymer)/(weight of carbon in monomer)). A methyl alcohol soluble fraction was removed in the calculation. [d] Viscosity-average molecular weight.

process[3] by examining the properties of the soluble polymers produced by the present method. Our previous studies on the properties of the polyaromatics were hindered by the lack of solvents to dissolve the polymers. Since poly(methylene) is soluble in suitable solvents, one can observe the NMR spectra of the polymers in solution and obtain crucial information concerning the end groups relevant to the polymerization mechanism. The data on the molecular weight of the polymers are also available because of the solubility of the polymers.

As an extension of our studies on dehalogenation polycondensation, we have carried out the polycondensation of 1,4-bis(bromomethyl)cyclohexane to give poly(1,4-cyclohexylene)(ethylene). This paper also includes results of this polycondensation.

Results and Discussion

Preparation of Poly(methylene). Table I summarizes results of the dehalogenation polycondensation of α,ω-dibromoalkanes. α,ω-Dibromoalkanes having five or more CH_2 units can be polymerized by using copper catalysts, but shorter α,ω-dibromoalkanes (1,4-dibromobutane, 1,3-dibromopentane, and 1,2-dibromoethane) did not give the polymer due to instabilities of their Grignard reagents.[2f] In the case of 1,5-dibromopentane, its Grignard reagent has some stability at room temperature. However, the polycondensation of 1,5-dibromopentane at room temperature gave only an oily low molecular weight poly(methylene). Carrying out the polycondensation at a lower temperature gave solid poly(methylene) albeit in a low yield (experiment 2).

Various copper catalysts listed in Table I have catalytic activities for the dehalogenation polycondensation of 1,6-dibromohexane at room temperature, giving poly(methylene) in yields ranging from 40 to 84%. In contrast to occurrence of the facile polymerization of 1,6-dibromohexane, 1,6-diiodo- and 1,6-dichlorohexane did not give the polymer. Among the copper catalysts tested, $CuBr(PPh_3)$[5] (PPh_3 = triphenylphosphine) gives poly(methylene) having the highest melting point. The observation that $CuBr$-(PPh_3) has much higher catalytic activities than fully coordinated $CuBr(PPh_3)_3$ (experiment 8) suggests the importance of the presence of vacant coordination site(s) on Cu. Formation of $MgBr_2$ in the polycondensation (eq 5) was confirmed by powder X-ray analysis of the product.

Silver compounds, $AgNO_3$ (experiment 9) and AgBr, showed some catalytic activities, but the yields as well as melting points of poly(methylene) obtained were low. A nickel compound, $NiCl_2(bpy)$, which is one of the most
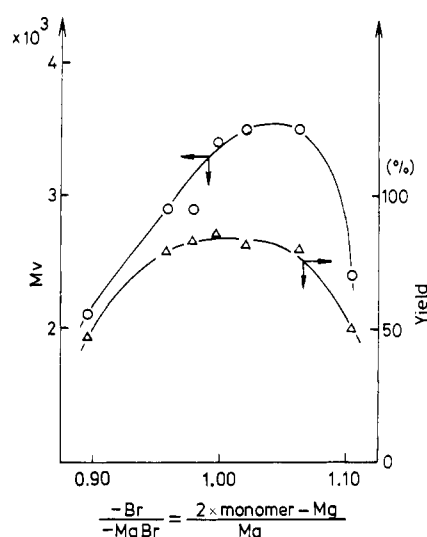
Figure 1. Effect of the amount of Mg on the molecular weight (O) and yield (Δ) of poly(methylene). Monomer = 1,6-dibromohexane. Polymerization was carried out at room temperature.

active catalysts in dehalogenation polycondensation of dihalo aromatic compounds showed no activity for the present polycondensation of α,ω-dibromoalkanes.

In order to characterize the present polycondensation, we have carried out the polycondensation of 1,6-dibromohexane and 1,12-dibromododecane (about 50 times) under various reaction conditions by using the most effective catalyst, $CuBr(PPh_3)$. The following features of the polycondensation emerge from these experiments.

(i) Temperature: If the polymerization is carried out at low temperatures ranging from -10 to +25 °C, little effect of the polymerization temperature on the yield and melting point of the polymer is observed. However, carrying out the polymerization at the boiling point of THF (66 °C) did not give the polymer, probably due to thermal instabilities of Cu–alkyl compounds formed as active intermediates of the catalytic reaction (vide infra).

(ii) Amount of Mg: Figure 1 shows the effect of the amount of Mg on the yield and molecular weight of poly(methylene) obtained by the polymerization of 1,6-dibromohexane. The yield decreases when the molar ratio of Mg to monomer deviates from unity, in accord with the theory of polycondensation. However, the highest molecular weight for poly(methylene) seems to be obtained at a slight stoichiometric excess of Mg. This may be due

to consumption of a part of the Grignard reagent in alkylation of the Cu catalyst (Scheme I; vide infra) or incompletion of the Grignard reagent formation reaction.
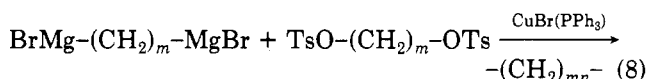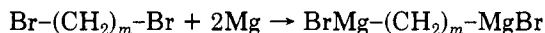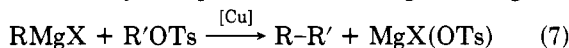
(iii) Amount of CuBr(PPh₃): There is a trend that the yield of poly(methylene) increases with an increase in the amount of CuBr(PPh₃). The melting point of the polymer also becomes higher on increasing the amount of CuBr-(PPh₃). However, the effect of the amount of CuBr(PPh₃) is minor if more than 1 mol % of the catalyst per Br-$(CH_2)_6$-Br is added. In the presence of more than 1 mol % of CuBr(PPh₃) per monomer, the yield of the polymer is greater than 70% and the polymer obtained has a melting point higher than 120 °C. On the contrary, when the amount of the catalyst is less than 1 mol %, the yield and the melting point are considerably lowered. For example, addition of only 0.01 mol % of CuBr(PPh₃) per Br-$(CH_2)_6$-Br gives only 44% yield, and the poly(methylene) thus obtained has a low melting point of 99 °C.

(iv) THF is a better solvent than other ethereal solvents such as diethyl ether and diglyme.

In relation to the dehalogenation polycondensation described above, we have tried the following two other types of polycondensation: (a) polycondensation of Br-$(CH_2)_6$-Br using Li, instead of Mg, as the dehalogenation reagent

$$Br-(CH_2)_6-Br + 2Li \xrightarrow{CuBr(PPh_3)} -(CH_2)_{6n}- \quad (6)$$
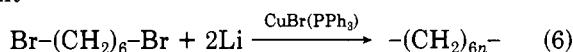
(this polycondensation also affords poly(methylene), but the yield (5%) and the melting point (98 °C) of the poly(methylene) obtained were low); and (b) polycondensation utilizing a copper-catalyzed C–C coupling between a p-toluenesulfonyl compound and the Grignard reagent[6]

$$RMgX + R'OTs \xrightarrow{[Cu]} R-R' + MgX(OTs) \quad (7)$$

$$OTs = -SO_2C_6H_4CH_3$$

$$Br-(CH_2)_m-Br + 2Mg \rightarrow BrMg-(CH_2)_m-MgBr$$

$$BrMg-(CH_2)_m-MgBr + TsO-(CH_2)_m-OTs \xrightarrow[-(CH_2)_{mn}-]{CuBr(PPh_3)} \quad (8)$$

$$m = 6, 12$$

The yield of this polycondensation (ca. 80%) and the melting point (120–121 °C) of the poly(methylene) prepared according to this method are comparable with the yield and the melting point of the dehalogenation polycondensation expressed by eq 5.

Reaction Mechanism. In order to provide the basis for characterization of the poly(methylene), we discuss here the mechanism of the copper-catalyzed dehalogenation polycondensation of Br-$(CH_2)_m$-Br with Mg.

The polycondensation evidently proceeds through the C–C coupling between the alkyl halides and the Grignard reagents formed in the reaction mixture. The reaction of Br-$(CH_2)_m$-Br with an equimolar amount of Mg does not give the sole product Br-$(CH_2)_m$-MgBr, as shown in eq 2, but the reaction gives a mixture of BrMg-$(CH_2)_m$-MgBr, Br-$(CH_2)_m$-MgBr, and intact Br-$(CH_2)_m$-Br.[7] However, if an equimolar amount of Mg to Br-$(CH_2)_m$-Br is added, the ratio between the two functional groups MgBr and Br is maintained at unity and thus the polycondensation proceeds without losing the stoichiometric relationship required for the polycondensation.
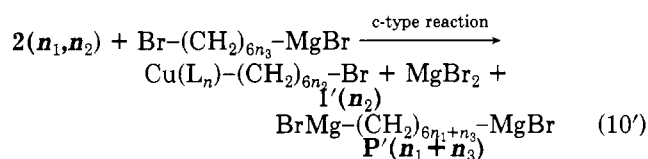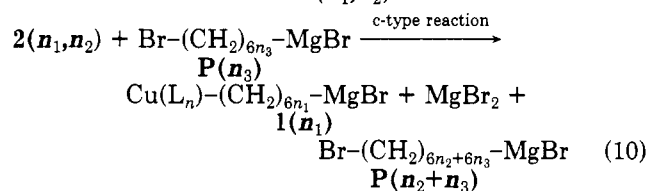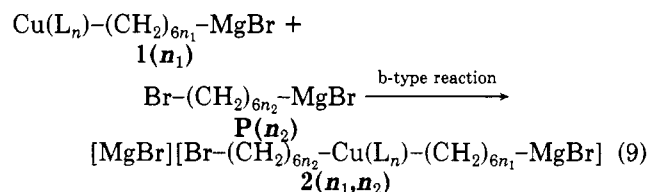
One of the possible mechanisms of the copper-catalyzed C–C coupling between RMgBr and R'Br is comprised of the following elementary steps: (a) formation of an alkylcopper intermediate, Cu(L_n)R (L = ligand like PPh₃ or THF), by the reaction of Cu(L_n)X with RMgBr (several examples of the preparation of alkylcopper(I) complexes

by alkyl exchange reactions between copper salts and main-group metal-alkyl compounds, including the Grignard reagent, have been reported[2a,h,8]); (b) further alkylation of Cu(L_n)R by RMgBr to give a cuprate intermediate, [MgBr][Cu(L_n)R₂] (formation of this type of cuprate compound in reactions of copper salts with main-group metal-alkyl compounds has also been reported[2a,8a,9]); and (c) elimination of R–R' with formation of Cu(L_n)R and MgBr₂ in the reaction of [MgBr][Cu(L_n)R₂] with R'Br (selective formation of the C–C coupling product R–R' in the reaction of dialkylcuprate, [cation][CuR₂], with organic halide, R'X, has been reported[8a,9]).
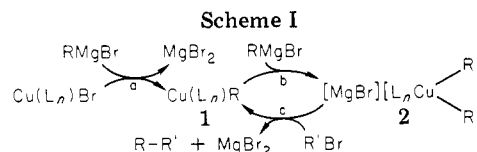
Scheme I

If this mechanism can be applied to the present polycondensation of 1,6-dibromohexane, the propagation reaction is expressed as follows:

Scheme II

$$Cu(L_n)-(CH_2)_{6n_1}-MgBr +$$
$$\mathbf{1(n_1)}$$
$$Br-(CH_2)_{6n_2}-MgBr \xrightarrow{\text{b-type reaction}}$$
$$\mathbf{P(n_2)}$$
$$[MgBr][Br-(CH_2)_{6n_2}-Cu(L_n)-(CH_2)_{6n_1}-MgBr] \quad (9)$$
$$\mathbf{2(n_1,n_2)}$$

$$2(n_1,n_2) + Br-(CH_2)_{6n_3}-MgBr \xrightarrow{\text{c-type reaction}}$$
$$\mathbf{P(n_3)}$$
$$Cu(L_n)-(CH_2)_{6n_1}-MgBr + MgBr_2 +$$
$$\mathbf{1(n_1)}$$
$$Br-(CH_2)_{6n_2+6n_3}-MgBr \quad (10)$$
$$\mathbf{P(n_2+n_3)}$$

$$2(n_1,n_2) + Br-(CH_2)_{6n_3}-MgBr \xrightarrow{\text{c-type reaction}}$$
$$Cu(L_n)-(CH_2)_{6n_2}-Br + MgBr_2 +$$
$$\mathbf{1'(n_2)}$$
$$BrMg-(CH_2)_{6n_1+n_3}-MgBr \quad (10')$$
$$\mathbf{P'(n_1+n_3)}$$

etc.

where $\mathbf{P(n)}$ (or $\mathbf{P'(n)}$) stands for the polymer having $6n$ methylene units and $\mathbf{1(n)}$ (or $\mathbf{1'(n)}$) and $\mathbf{2(n_i,n_j)}$ represent the active intermediate copper complexes 1 and 2 having alkyl ligand(s) with the corresponding chain length.

If the active alkylcopper species $\mathbf{1(n)}$ and $\mathbf{2(n_i,n_j)}$ have sufficiently high thermal stabilities in solution, no special termination reaction will proceed, and the polymer will contain only CH₂Br and CH₂MgBr groups as the terminal groups (the latter group is converted into a CH₃ group during workup of the polymer). However, it is known that the alkylcopper species, especially the neutral complex of type 1, do not have very high thermal stabilities and sometimes undergo a β-elimination reaction to give olefin and a CuH species, which further undergoes a coupling reaction with the alkylcopper complex to release RH:[8,10]
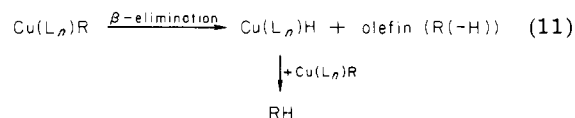
If this β-elimination reaction proceeds in the present polycondensation, the polymer obtained after the workup will contain a CH=CH₂ group as the terminal group, in addition to the CH₂Br and CH₃ groups. On the basis of the
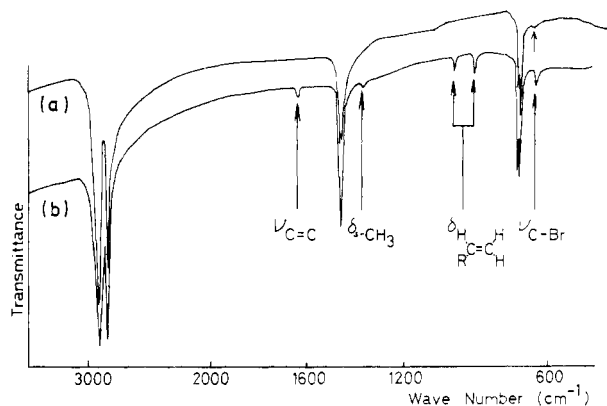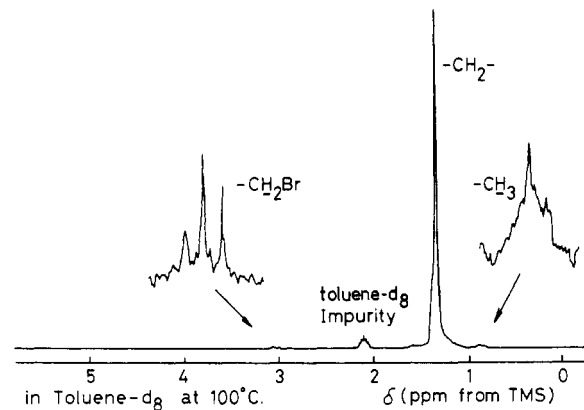
Figure 2. IR spectra of the poly(methylenes) prepared by using (a) $CuBr(PPh_3)$ (expt 4) and (b) CuBr (expt 5).

Figure 3. ^1H-NMR spectrum of the poly(methylene) prepared with $CuBr(PPh_3)$.

Figure 4. GPC curve of the poly(methylene) (solid line). The chain line shows the most probable distribution curve calculated by assuming the extent of reaction equals 0.975.

reaction mechanism shown above, we now discuss the characterization and properties of the poly(methylene) obtained.

IR and NMR Spectra. Figure 2 shows IR spectra of poly(methylenes) prepared by the polycondensation of $Br-(CH_2)_6-Br$ using $CuBr(PPh_3)$ (experiment 4) or CuBr (experiment 5) as the catalyst. The IR spectrum of the poly(methylene) prepared with $CuBr(PPh_3)$ (Figure 2a) is essentially the same as that of linear poly(ethylene) prepared with a Ziegler catalyst, showing $\nu(C-H)_{asym}$ at 2910 cm^{-1}, $\nu(C-H)_{sym}$ at 2850 cm^{-1}, CH_2 scissoring vibration bands at 1473 and 1462 cm^{-1}, and CH_2 rocking vibration bands at 730 and 720 cm^{-1}.[11a-c] A $\nu(C-Br)$ band at 640 cm^{-1} due to the terminal CH_2Br group is also observable in the IR spectrum, but the intensity of the band is very weak. Although the poly(methylene) has the terminal CH_3 group as proved by NMR, $\delta(CH_3)$ due to the CH_3 group is not observable in the spectrum. The IR spectrum of the poly(methylene) prepared with $CuBr(PPh_3)$ shows no peak due to the terminal $CH=CH_2$ group, which may be formed by the β-elimination (eq 11).

In contrast to the IR spectrum of the poly(methylene) prepared with $CuBr(PPh_3)$, that of the poly(methylene) prepared with CuBr (Figure 2b) shows bands assignable to the terminal $CH=CH_2$ group at 1600 ($\nu(C=C)$), 985 ($\delta(C-H)$), and 900 cm^{-1} ($\delta(C-H)$), indicating that the active alkylcopper intermediate $(1(n))$ or $2(n_i,n_j))$ formed in the polycondensation with CuBr does not have a high thermal stability and thus undergoes the β-elimination reaction whereas the active alkylcopper intermediate formed in the polycondensation with the phosphine-coordinated complex, $CuBr(PPh_3)$, has a higher thermal stability. This conclusion, obtained by comparing the two IR spectra, is obviously related to the lower melting point of the poly-(methylene) obtained in the polycondensation with CuBr (experiment 5). It has been reported that the PPh_3 ligand has the effect of stabilizing thermally unstable alkylcopper compounds.[8] IR spectra of both of the poly(methylenes) show no peak due to branching of the polymer.[11c,d]

Figure 3 shows the ^1H-NMR spectrum of the poly-(methylene) prepared by the $CuBr(PPh_3)$-catalyzed poly-condensation of $Br-(CH_2)_6-Br$ (experiment 4). Besides a strong singlet peak of the CH_2 protons in the main chain, the spectrum shows weak peaks assignable to the terminal CH_3 (δ 0.91, triplet or multiplet) and CH_2Br (δ 3.06, triplet, $^3J(H-H)$ = 7 Hz). The assignment of the peaks of the terminal CH_3 and CH_2Br groups was made by comparing the spectra of the polymers with that of $CH_3-(CH_2)_{11}-Br$. The relative intensity of the CH_3 signal to that of the CH_2Br signal in Figure 3 indicates that the number of CH_3 terminal groups in the polymer is almost the same as that
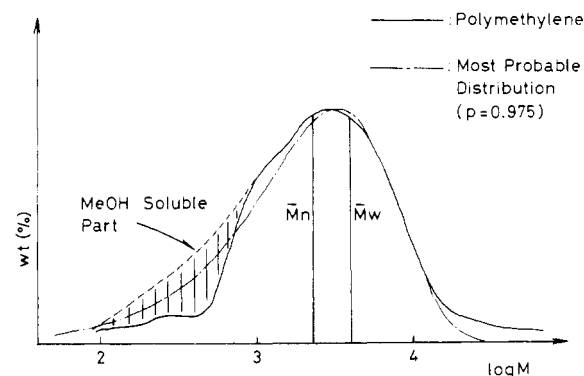
of the CH_2Br terminal groups. Relative peak areas of the CH_3 and CH_2Br signals to the peak area of the CH_2 signal roughly agree with the molecular weight of the poly-(methylene). Although the ^1H-NMR spectrum of the poly(methylene) prepared with $CuBr(PPh_3)$ as the catalyst does not show peaks due to olefinic protons, that of the poly(methylene) prepared with CuBr shows additional signals at δ 5.0 and 5.9, which are assigned to the terminal olefinic protons formed according to eq 11.

Molecular Weight and Melting Point. The molecular weight (M_v = 3400) of the poly(methylene) prepared by the $CuBr(PPh_3)$-catalyzed polycondensation of $Br-(CH_2)_6-Br$ (experiment 4) corresponds to a degree of po-lymerization (DP) of about 40, demonstrating that the successive C-C coupling continues, on the average, about 40 times in the polycondensation. On the other hand, the successive C-C coupling in the $CuBr(PPh_3)$-catalyzed polycondensation of $Br-(CH_2)_{12}-Br$ continues less (about 22) times, affording a poly(methylene) having molecular weight almost the same as that of the poly(methylene) obtained in the $CuBr(PPh_3)$-catalyzed polycondensation of $Br-(CH_2)_6-Br$ (cf. experiments 4 and 13).

This observation that both of the polycondensations of the longer monomer, $Br-(CH_2)_{12}-Br$, and the shorter monomer, $Br-(CH_2)_6-Br$, give poly(methylenes) having almost the same molecular weight suggests that the upper limit of the molecular weight of the polymer is determined by the solubility of the polymer in the polymerization solvent.

Figure 4 shows a GPC (gel-permeation chromatography) curve of the poly(methylene) obtained in experiment 11 (M_v = 2900). If we take into account that a part of the lower molecular weight fraction is removed as a metha-nol-soluble fraction during workup of the polymer,[12] we
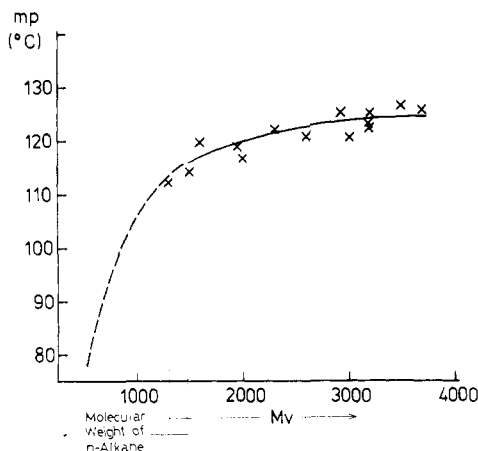
Figure 5. Relation between mp and M_v of the poly(methylene). Data obtained in the present study are shown by ✕. The broken line shows the relation between mp and molecular weight of isolated $H-(CH_2)_n-H$.

are led to the conclusion that the GPC curve in Figure 4 roughly agrees with the most probable distribution curve calculated according to the theory of polycondensation[13] with a p value (degree of reaction) of 0.975. The number-average molecular weight, M_n, and weight-average molecular weight, M_w, of the polymer are calculated as 2300 and 3900, respectively, from the GPC curve shown in Figure 4. The GPC data also show that the poly(methylene) contains a fraction having a molecular weight higher than 10 000 (corresponding to DP $\simeq$ 120), although the amount of the fraction is small.

From the viscosity-average molecular weights, M_v, and melting points, mp, of various poly(methylenes) prepared in the present study, we obtained a relationship between the two values as shown in Figure 5. The curve showing the relationship between M_v and the melting point smoothly joins with a curve showing the relation between the molecular weight of pure $H-(CH_2)_n-H$ and the melting point of the compound.[14]

When the poly(methylene) is treated with $LiAlH_4$, a considerable part (ca. $^2/_3$) of the terminal CH_2Br group is reduced to a CH_3 group as judged from decrease in the Br content of the polymer

$$CH_2Br + LiAlH_4 \rightarrow CH_3 \tag{12}$$
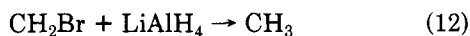
The polymer treated with $LiAlH_4$ shows same melting point and M_v as those of the untreated polymer within experimental error, showing that the terminal CH_2Br does not affect the melting point and solution viscosity of the polymer. The $\nu(C-Br)$ band in the IR spectrum as well as the CH_2Br signal in the ^1H-NMR spectrum became unobservable after treatment of the polymer with $LiAlH_4$. In spite of the occurrence of reaction 12, the CH_2Br group was not quaternarized by amines.

Other Physical Properties and Crystallinity of Poly(methylene). The poly(methylene) prepared in this study has a heat of fusion of 180 J/g as determined by differential scanning calorimetry. If the relation between the heat of fusion and degree of crystallinity of poly(ethylene) proposed by Fischer and Hinrichsen[15] can be applied to the present poly(methylene), the degree of crystallinity of the poly(methylene) is calculated as 85%. The $LiAlH_4$-treated poly(methylene) has a somewhat higher heat of fusion, 205 J/g, a value corresponding to a degree of crystallinity of 96%. The poly(methylene) has a density of 1.017 before treatment with $LiAlH_4$, but the density decreases to 0.979 on treating the polymer with $LiAlH_4$, showing that the effect of Br in the terminal
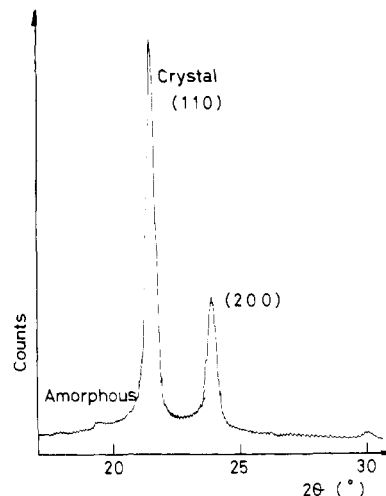
Figure 6. X-ray diffraction pattern of the poly(methylene). X-ray = Cu Kα.

CH_2Br group on the density of the polymer is not negligible. The value of $\rho = 0.979$ corresponds to a degree of crystallinity of 81% according to the reported relation between the density and the degree of crystallinity of poly(ethylene).[16]

The high crystallinity of the poly(methylene) suggested by its heat of fusion and density is also confirmed by IR spectroscopy and, more directly, by the powder X-ray diffraction pattern of the polymer. As described above, the IR spectrum shows two CH_2 rocking vibration bands at 730 and 720 cm^{-1}, and it has been reported that one can estimate the degree of crystallinity of poly(ethylene) by comparing relative intensities of the bands at 730 and 720 cm^{-1}.[11] The degree of crystallinity estimated by comparing the intensities of the two bands is 72%. The relative intensities of the two bands were virtually unchanged on treatment with $LiAlH_4$. Figure 6 shows the X-ray diffraction pattern of the powdery poly(methylene) (Cu Kα X-rays). The diffraction pattern shows a strong (110) diffraction band at $2\theta = 21.4°$ and (200) band at 23.7°. The diffraction pattern shows also a broad band due to an amorphous part of the polymer at $2\theta = 19.5°$.[17] The degree of crystallinity estimated from the relative intensities of the crystalline and amorphous diffraction bands[17] is 91%. After treatment with $LiAlH_4$, the value slightly increases to 92%.

The degree of crystallinity of the poly(methylene) estimated by the various methods is comparable to or higher than even that of commercially available high-density poly(ethylene) prepared by the Ziegler method, although the difference in the molecular weights of the two polymers should be considered, since it may bring about the difference in the structure of the microcrystals of the two polymers. For example, the X-ray diffraction bands shown in Figure 6 are considerably sharper than that observed with the commercially available high-density poly(ethylene), and the broad band at $2\theta = 19.5°$ observed in the X-ray diffraction pattern of the commercially available high-density poly(ethylene) is stronger than that observed in Figure 6.

According to the reaction process to produce the present poly(methylene) discussed above, the poly(methylene) is expected to have a linear structure and contain no branch such as that contained in low-density poly(methylene). The high crystallinity of the present poly(methylene) is apparently related to its linear structure.

Application of the Polycondensation to Dibromides of Cycloalkanes. *trans*-1,4-Bis(bromomethyl)cyclohexane

can be polymerized by the Cu-catalyzed polycondensation technique to afford a thermally stable material in good yield
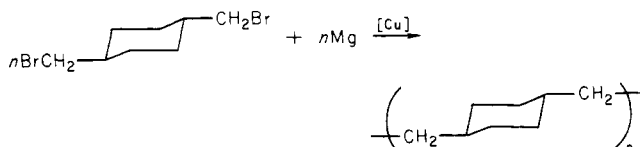
IR and NMR spectra (see Experimental Section) of the polymer confirm the formation of the polymer shown above. However, the presence of the terminal CH$_2$Br unit in a considerable proportion as revealed by ^{1}H-NMR spectroscopy indicates that the polymer, poly(*trans*-1,4-cyclohexylene)(ethylene), has only a low molecular weight ($M_n \simeq 1000$).[18] It is reported that reactions of dialkylcuprates with *sec*-alkyl bromides (RBr) proceed with inversion of configuration in R.[8a] The backside attack implied could be substantially slowed by branching at C$_\beta$ as in 1,4-bis(bromomethyl)hexane.

The polymer was fractionated by extraction with boiling *p*-xylene, and a *p*-xylene-insoluble fraction had an extremely high thermal stability, showing no softening up to 250 °C and no degradation up to 400 °C under N$_2$ (thermogravimetric analysis). The high thermal stabilities are consistent with the known fact that polymers containing the 1,4-cyclohexylene unit (e.g., polyesters[19] containing the unit) have high thermal stabilities. The powder X-ray diffraction pattern (Cu Kα X-rays) of the polymer shows sharp diffraction bands at $2\theta = 19.7°$ and $18.0°$. The polymer has lower solubilities compared with the poly(methylene), presumably due to its high crystallinity as suggested by its linear and rigid structure demonstrated by the CPK molecular model. This low solubility of the polymer accounts for termination of the polymerization before the polymer gains a larger molecular weight.

In contrast to *trans*-1,4-bis(bromomethyl)cyclohexane, its cis isomer, *cis*-1,4-bis(bromomethyl)cyclohexane, did not give the corresponding polymer by the Cu-catalyzed polycondensation technique, probably due to instability of its Grignard reagent (there seems to be a chance that the CH$_2$Br and CH$_2$MgBr groups have an intramolecular interaction to undergo an intramolecular C–C coupling reaction). 1,4-Dibromocyclohexane was not polymerized, either. This seems to derive from the inefficiency of the reaction of dialkylcuprate with secondary bromides.[20]

Experimental Section

Material. Commercially available α,ω-dihaloalkanes purchased from Tokyo Kasei Co. Ltd. or Wako Co. Ltd. were purified by distillation except for 1,12-dibromododecane, which was purified by recrystallization from methyl alcohol. *trans*-1,4-Bis(bromomethyl)cyclohexane and *cis*-1,4-bis(bromomethyl)cyclohexane were prepared according to the method of Haggis and Owen.[21] CuBr, CuCl, CuBr$_2$, and AgNO$_3$ were used as purchased. CuBr(PPh$_3$),[21] CuBr(PPh$_3$)$_3$,[22] and NiCl$_2$(bpy)[23] were prepared according to methods described in the literature. TsO–(CH$_2$)$_m$–OTs (OTs = *p*-SO$_2$C$_6$H$_4$CH$_3$; *m* = 6, 12) was prepared by reaction between HO–(CH$_2$)$_m$–OH and *p*-toluenesulfonyl chloride in pyridine at 0 °C. About 2.2 mol of *p*-toluenesulfonyl chloride per mole of the diol was added: yield, ca. 70%. They had high purities as revealed by elemental analysis and NMR spectroscopy. Granular magnesium was activated by agitation under N$_2$ for 1 day. Solvents were dried over Na, distilled under N$_2$, and stored under N$_2$.

Polycondensation (cf. Table I). All polymerizations were carried out under N$_2$.

Experiment 4. When 59 mg (0.15 mmol) of CuBr(PPh$_3$) was added to a mixture of products obtained by the reaction of 3.536 g (14.5 mmol) of 1,6-dibromohexane with 0.354 g (14.5 mmol) of

Mg in dry tetrahydrofuran (29 cm^3), a smooth polycondensation started to give a white precipitate of poly(methylene). The polymerization was almost completed in 1–2 h at room temperature. After the reaction mixture was stirred for a further 10 h, it was poured into 500 cm^3 of methyl alcohol, and the polymer precipitated was collected over a glass filter. The crude polymer was dissolved in hot toluene and purified by reprecipitation after filtration of the solution to yield 1.000 g of white poly(methylene). Anal. Found: C, 82.2; H, 14.5; Br, 3.2. Calcd for –(CH$_2$)–: C, 85.7; H, 14.3. Melting point and other physical properties are described in the text and in Table I. Other polymerizations of α,ω-dihaloalkanes were carried out analogously.

Copolymerization of Br–(CH$_2$)$_m$–Br and TsO–(CH$_2$)$_m$–OTs. CuBr(PPh$_3$) (49 mg, 0.12 mmol) and TsO–(CH$_2$)$_{12}$–OTs (3.064 g, 6.00 mmol) were added at 0 °C into a THF (30 cm^3) solution of di-Grignard reagent formed by reaction of Br–(CH$_2$)$_m$–Br (1.989 g, 6.00 mmol) and magnesium (0.293 g, 12.1 mmol). The reaction temperature was gradually raised to room temperature. After the reaction mixture was stirred for 15 h at room temperature, it was poured into HCl-acidic methyl alcohol, and the polymer precipitated was collected over a glass filter. The polymer was dissolved in hot toluene and purified by reprecipitation after filtration of the solution to yield 1.67 g (theoretical yield of the polymer having infinite length, 2.02 g) of a white poly(methylene): mp 120–121 °C. Copolymerization between Br–(CH$_2$)$_6$–Br and TsO–(CH$_2$)$_6$–OTs was carried out analogously.

Reduction of CH$_2$Br with LiAlH$_4$. The poly(methylene) (200 mg, 7.2% Br content) prepared by using CuBr was dissolved in 30 cm^3 of toluene at 90 °C under an atmosphere of N$_2$. LiAlH$_4$ (0.68 g) was added to the solution, and after the reduction was carried out for 1 h at 90 °C, methyl alcohol was added to the reaction mixture to destroy excess LiAlH$_4$. Polymer thus obtained was washed repeatedly with dilute hydrochloric acid, collected by filtration, and purified by reprecipitation. The bromine content decreased to 2.7%. The reduction of the poly(methylene) prepared by using CuBr(PPh$_3$) was carried out analogously.

Polymerization of *trans*-1,4-Bis(bromomethyl)cyclohexane. A mixture of *trans*-1,4-bis(bromomethyl)cyclohexane (2.023 g, 7.5 mmol), magnesium (0.182 g, 7.5 mmol), and THF (3 cm^3) was stirred at room temperature. After 30 min, when all of magnesium was consumed to give the Grignard reagent, CuBr(PPh$_3$) (30 mg, 0.074 mmol) was added to initiate the polycondensation. After 48 h of stirring at room temperature, the reaction mixture was poured into HCl-acidic methyl alcohol (500 cm^3), and the polymer precipitated was collected over a glass filter and dried under vacuum to yield 0.418 g of white poly(*trans*-1,4-cyclohexylene)(ethylene). For analytical data, see ref 18. IR (KBr, cm^{-1}): 2900 (s), 2850 (s), 1450 (s) (δ(CH$_2$)), 1230 (w), 940 (w), 890 (w), 640 (w) (ν(C–Br)). ^{1}H NMR (*o*-dichlorobenzene, 100 °C): δ 0.8–1.3 (12 H, m, CH$_2$ in cyclohexylene and the CH$_2$CH$_2$ group), 18 (2 H, m, methine proton in the cyclohexylene ring), 3.2 (doublet, 6 Hz, CH$_2$Br).

Instruments. IR spectra were recorded on a Hitachi Model 295 infrared spectrometer. X-ray diffraction patterns were obtained with a Phillips PW-1051 X-ray diffractometer. Microanalysis of C and H was performed by Mr. T. Saito of our research laboratory with a Yanagimoto CHN autocorder. Melting point, heat of fusion, and thermal stability of the polymers were measured by a Shimadzu DT-30 thermal analyzer. GPC analysis was performed with a Shodex LC HT3 gel-permeation chromatograph. Viscosity was measured with an Ubbelohde viscometer. A literature equation was applied to calculate M_v of poly(methylene).[24]

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(18) The relative intensity of the peak assigned to the CH₂Br group (δ 3.2 ppm, doublet (7 Hz)) to that assigned to the CH group (δ 1.8 ppm) in the recurring unit is about 1:7.8. This ratio corresponds to a formulation of H–(CH₂C₆H₁₀CH₂)₇.₈–Br ($\bar{M}_n$ = 930) if one assumes that the polymer contains, on the average, one CH₂Br as the terminal groups. The formulation roughly agrees with analytical data of the polymer (Found: C, 77.9; H, 12.2; Br, 9.0. Calcd: C, 79.7; H, 11.7; Br, 8.5).

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Synthesis and Properties of Poly[N-(1,1-dimethyl-3-oxobutyl)acrylamide oxime][†]

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ABSTRACT: The synthesis and properties of poly[N-(1,1-dimethyl-3-oxobutyl)acrylamide oxime] are described for the first time. The polymer is readily prepared by direct oximation of the polymeric ketone. The polymeric oxime is a stable, glassy polymer that is soluble in alkali at pH values above 12.5. Both the amide and oximate ion functional groups are stable in aqueous alkali for periods of over 1 year. These conclusions are based upon detailed studies of polymer solutions with ¹³C NMR.

Introduction

In our laboratory we were seeking a polymer that would be soluble and stable in highly alkaline, aqueous solutions but that would be insoluble, optically clear, and water insensitive at pH values below 10–12. Poly[N-(1,1-dimethyl-3-oxobutyl)acrylamide], which is commonly referred to as polydiacetoneacrylamide (PDAA), is a very

interesting glassy polymer that is readily available from monomeric DAA, which has been described.[1-3] We decided to investigate the synthesis and resulting properties of PDAA oxime in the hope that the oxime functional group would confer the desired chemical and physical properties.

A literature search revealed that DAA oxime monomer, although mentioned, was said not to copolymerize with DAA.[4] A patent on DAA oxime does not mention vinyl polymerization but is directed to its use as a reagent for epoxy resin curing.[5] The isocyanate derivatives of PDAA oxime have been reported.[6] In that work, the PDAA oxime was prepared by oximation of PDAA as an intermediate,

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