

Mechanical Properties of Substituted Polyacetylenes

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ABSTRACT: The tensile and dynamic mechanical properties of substituted polyacetylenes, which are stable in air at room temperature, were studied. Tensile measurements at 25 °C showed that polyacetylenes with a phenyl group are generally hard and brittle, whereas those with a long *n*-alkyl group are soft and ductile. This substituent effect resembles that for vinyl polymers. According to dynamic mechanical measurement at -150 to +200 °C, most polyacetylenes have glass transition temperatures around 200 °C that do not strongly depend on the kinds of substituents. This result contrasts with the T_g of vinyl polymers which are much lower and vary widely with the kinds of substituents. It is concluded that the T_g of polyacetylenes is mainly governed by the alternating double bond structure of the main chain.

Introduction

Since polyacetylene shows metallic conductivity on doping, its chemistry and physics have been the subject of intensive research. Regarding its tensile properties, *cis*-polyacetylene is soft and ductile.^{1,2} According to the dynamic mechanical test, polyacetylene has a glass transition temperature (T_g) above 150 °C, indicating that the motion of the polymer chain is remarkably restricted.³ Polyacetylene is easily oxidized in air, which causes deterioration of its mechanical properties.^{2,3b}

We have found that group 5 and 6 transition-metal catalysts are effective for the polymerization of substituted acetylenes and have synthesized a number of new, high molecular weight substituted polyacetylenes.⁴ Unlike polyacetylene, these substituted polyacetylenes undergo neither oxidation nor molecular weight decrease in air at room temperature⁵ because their main chains have twisted conformations owing to the substituents. Substituted polyacetylenes have good gas permeability,⁶ photoconductivity,⁷ and radiodegradability⁸ and may therefore become new specialty polymers. The mechanical properties of these polyacetylenes, however, are hardly known.

The mechanical properties of a polymer are important to its practical use. It therefore seemed of interest to us to study the mechanical properties of these substituted polyacetylenes, including the influence of substituents and comparison with analogous vinyl polymers.

We here report on the tensile behavior and dynamic viscoelasticity of substituted polyacetylenes prepared from aromatic, aliphatic, and heteroatom-containing disubstituted acetylenes and several monosubstituted acetylenes. These polymers are all stable in air at room temperature, soluble, and film-forming. Young's moduli, elongations at break, and T_g 's of the polyacetylenes have been determined. Substituent effects on mechanical properties are discussed and compared with those for vinyl polymers.

Experimental Section

Substituted polyacetylenes were prepared by using group 5 and 6 transition-metal catalysts from the following monomers: aromatic acetylenes, $\text{PhC}\equiv\text{CR}^9$ ($\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_6\text{H}_{13}$); aliphatic acetylenes, $\text{CH}_3\text{C}\equiv\text{CR}^{10}$ ($\text{R} = n\text{-C}_3\text{H}_7$, $n\text{-C}_8\text{H}_{11}$, $n\text{-C}_7\text{H}_{15}$), $\text{HC}\equiv\text{CC}(\text{CH}_3)_2$;¹¹ Cl-containing acetylenes, $\text{ClC}\equiv\text{CPh}$,¹² $\text{ClC}\equiv\text{CR}^{13}$ ($\text{R} = n\text{-C}_4\text{H}_9$, $n\text{-C}_8\text{H}_{13}$, $n\text{-C}_8\text{H}_{17}$); Si-containing acetylenes, $\text{CH}_3\text{C}\equiv\text{CSi}(\text{CH}_3)_2\text{R}$ [$\text{R} = \text{CH}_3$,¹⁴ $n\text{-C}_6\text{H}_{13}$,¹⁵ $\text{CH}_2\text{Si}(\text{CH}_3)_3$,¹⁶ $\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$,¹⁶], $\text{HC}\equiv\text{CCH}[\text{Si}(\text{CH}_3)_3]\text{R}^{17}$ ($\text{R} = n\text{-C}_5\text{H}_{11}$, $n\text{-C}_7\text{H}_{15}$). Details of the polymerizations are reported in ref 5 and/or each original reference.

Every polymer was obtained in over 50% yield and had a molecular weight of 10^5 – 10^6 . The *cis* content of poly(*tert*-butylacetylene) was ~75%,^{11b} while the geometric structures of the other polymers are unknown. The polyacetylenes were purified

by reprecipitation from toluene solution into methanol. Polymer films for the mechanical measurements were prepared by casting toluene solutions of polymers.

Tensile tests were carried out at 25 °C at a strain rate of 86% min^{-1} by using Tensilon, Model UTM-4L (Toyo Baldwin Co., Ltd.). A typical specimen was 35 mm in length, 10 mm in width, and 0.2 mm in thickness. Dynamic mechanical measurements were performed in a nitrogen atmosphere with Rheovibron, Model DDV-II-C (Toyo Baldwin Co., Ltd.). The oscillation frequency was 110 Hz, the temperature range -150 to +200 °C, and the heating rate 3 °C min^{-1} . A typical specimen was 50 mm in length, 3 mm in width, and 0.2 mm in thickness.

Results

Tensile Properties. Figure 1 shows stress-strain curves for polymers of aromatic disubstituted acetylenes. Poly-(1-phenyl-1-propyne) exhibits a high Young's modulus.¹⁸ Its elongation¹⁹ at break is no more than 5%, indicating that the polymer is very brittle. The tensile behavior of poly(1-chloro-2-phenylacetylene) resembles that of poly(1-phenyl-1-propyne). As the alkyl group of poly(1-phenyl-1-alkyne) becomes longer, Young's modulus tends to decrease. However, the elongations of poly(1-phenyl-1-alkynes) at break are all about 5% irrespective of the alkyl group length.

Figure 2 shows the stress-strain behavior of poly(2-alkynes). Young's modulus of poly(2-hexyne) is lower than that of poly(1-phenyl-1-propyne) (Figure 1), and its elongation at break is also about 5%. As the alkyl group becomes longer from poly(2-hexyne) to poly(2-octyne) and poly(2-decyne), Young's modulus decreases. Yield points are observed in both poly(2-octyne) and poly(2-decyne). The elongations of these two polyacetylenes at break are about 100% and 200%, respectively. Thus, as the alkyl group of a poly(2-alkyne) becomes longer, the polymer becomes softer and the more ductile. This contrasts with poly(1-phenyl-1-alkynes), in which the bulky phenyl group weakens the effect of alkyl-group length.

The tensile properties of poly(1-chloro-1-alkynes) are shown in Figure 3. These polymers behave similarly to poly(2-alkynes): as the alkyl group becomes longer, Young's modulus decreases and the elongation at break increases. The elongation of poly(1-chloro-1-decyne) at break is about 400%.

In Figure 4 are shown stress-strain curves for polymers of Si-containing disubstituted acetylenes. As is seen in the top figure, poly[1-(trimethylsilyl)-1-propyne] does not show a clear yield point and its stress increases monotonically with increasing strain. This suggests that the polymer chains gradually orient in the direction of elongation without causing any abrupt structural change. It is noteworthy that this polymer elongates appreciably (by ~70%) regardless

Table I
Tensile Properties of Substituted Polyacetylenes^a

sample no.	$-(\text{CR}_1=\text{CR}_2)_n-$		E , ^b MPa	σ_y , ^c MPa	γ_y , ^d %	σ_B , ^e MPa	γ_B , ^f %	$\int \delta^B \sigma d\gamma$, ^g MJ m ⁻³
	R ₁	R ₂						
1	Ph	CH ₃	2500			93	4.3	2.3
2	Ph	C ₂ H ₅	1100			57	5.8	1.9
3	Ph	<i>n</i> -C ₆ H ₁₃	700			23	4.2	0.6
4	Ph	Cl	2300			63	3.0	1.2
5	CH ₃	<i>n</i> -C ₈ H ₇	970			43	5.2	1.1
6	CH ₃	<i>n</i> -C ₅ H ₁₁	830	32	5.5	37	69	23
7	CH ₃	<i>n</i> -C ₇ H ₁₅	260	12	5.1	13	180	23
8	Cl	<i>n</i> -C ₄ H ₉	800			50	6.5	1.9
9	Cl	<i>n</i> -C ₆ H ₁₃	430	17	4.7	23	240	46
10	Cl	<i>n</i> -C ₈ H ₁₇	70			7	440	19
11	CH ₃	Si(CH ₃) ₃	630			40	73	20
12	CH ₃	Si(CH ₃) ₂ - <i>n</i> -C ₆ H ₁₃	270			13	49	6.3
13	CH ₃	Si(CH ₃) ₂ CH ₂ Si(CH ₃) ₃	500			27	26	5.3
14	CH ₃	Si(CH ₃) ₂ CH ₂ CH ₂ Si(CH ₃) ₃	800	25	4.7	33	33	9.7
15	H	C(CH ₃) ₃	600			20	3.4	0.4
16	H	CHSi(CH ₃) ₃ - <i>n</i> -C ₅ H ₁₁	630	28	5.1	27	11	2.3
17	H	CHSi(CH ₃) ₃ - <i>n</i> -C ₇ H ₁₅	530	16	3.5	27	90	20

^a At 25 °C, strain rate of 86% min⁻¹. ^b Young's modulus. ^c Yield stress. ^d Elongation at yield. ^e Tensile strength. ^f Elongation at break. ^g Energy to break (toughness).

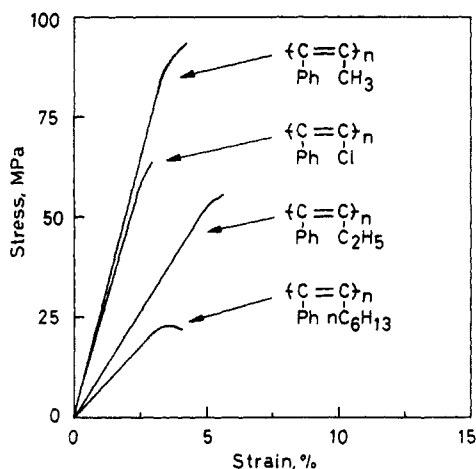


Figure 1. Stress-strain curves for polymers of aromatic disubstituted acetylenes (25 °C, 86% min⁻¹).

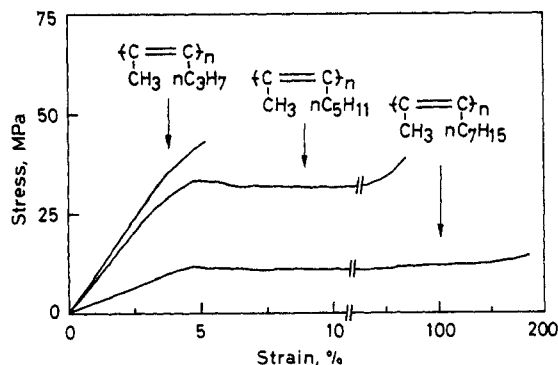


Figure 2. Stress-strain curves for poly(2-alkynes) (25 °C, 86% min⁻¹).

of the absence of a long alkyl group. Poly[1-(dimethyl-*n*-hexylsilyl)-1-propyne], which has a long alkyl group on the Si atom, shows a lower Young's modulus.

Results for the polyacetylenes with substituents containing two Si atoms are shown in the bottom of Figure 4. Young's moduli of these two polyacetylenes are similar to that of poly[1-(trimethylsilyl)-1-propyne], and their elongations at break (~30%) are somewhat smaller but

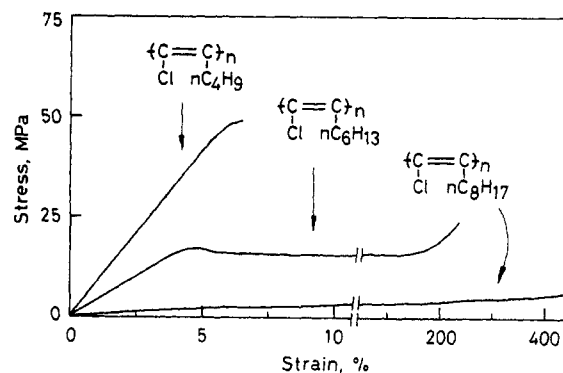


Figure 3. Stress-strain curves for poly(1-chloro-1-alkynes) (25 °C, 86% min⁻¹).

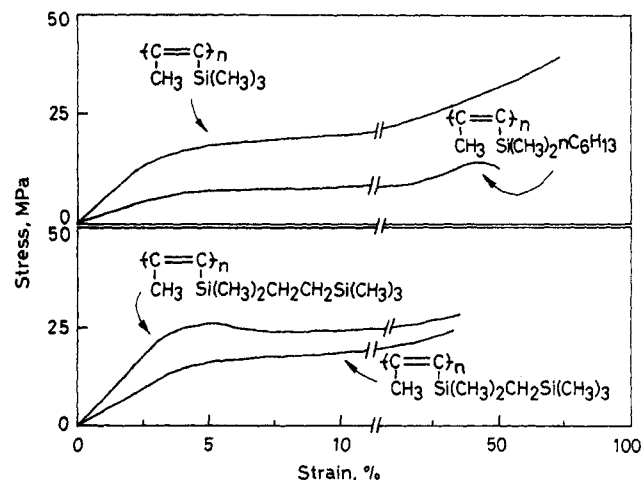


Figure 4. Stress-strain curves for poly(1-silyl-1-propynes) (25 °C, 86% min⁻¹).

not very different from that of poly[1-(trimethylsilyl)-1-propyne].

Among monosubstituted acetylene polymers, poly(*tert*-butylacetylene), which has the bulky and rigid *tert*-butyl group, is so brittle that its elongation does not exceed 4% (Figure 5). The elongation at break for poly[3-(trimethylsilyl)-1-octyne] is about 10%. Poly[3-(trimethylsilyl)-1-decyne] breaks at a higher strain (~90%). This

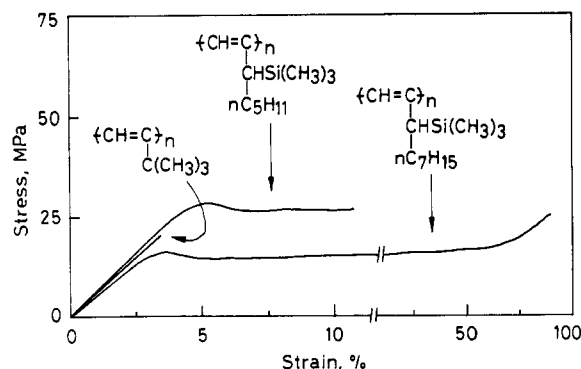


Figure 5. Stress-strain curves for monosubstituted acetylene polymers (25 °C, 86% min⁻¹).

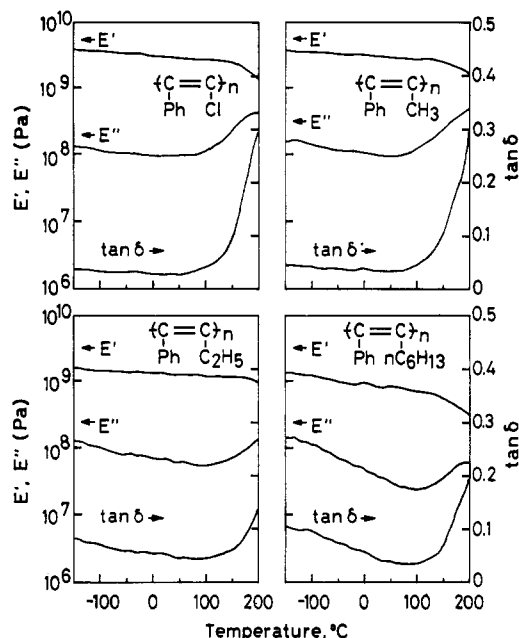


Figure 6. Dynamic viscoelasticity of polymers of aromatic disubstituted acetylenes (-150 to +200 °C, 110 Hz).

also demonstrates that the presence of a long alkyl group makes the polymer ductile.

Table I lists the tensile properties of substituted polyacetylenes.

Both Young's moduli (~2500 MPa) and tensile strengths (50–100 MPa) of poly(1-phenyl-1-propyne) and poly(1-chloro-2-phenylacetylene) are the highest among those of the substituted polyacetylenes examined. Young's modulus decreases as the alkyl group of poly(1-phenyl-1-alkyne) becomes longer. All these aromatic polyacetylenes break when elongated by only 5%; hence the energies required to break them (<2.5 MJ m⁻³) are small. Consequently, it appears that polyacetylenes containing a phenyl group are hard and brittle. Poly(*tert*-butylacetylene) is also so brittle that it can be elongated only slightly.

Poly(2-alkynes) that have long alkyl groups like *n*-pentyl and *n*-heptyl show relatively low Young's moduli (≤830 MPa) and low tensile strengths (10–40 MPa). These polyacetylenes elongate up to 70–180%, and the energies to break them (~23 MJ m⁻³) are fairly large. Thus, these polyacetylenes are soft and ductile. Poly(1-chloro-1-alkynes) with long alkyl groups such as *n*-hexyl and *n*-octyl show the same properties.

Young's moduli and elongations at break of Si-containing polyacetylenes are similar to aliphatic polyacetylenes rather than to aromatic polyacetylenes. However, the elongations of these polymers at break are not so large as

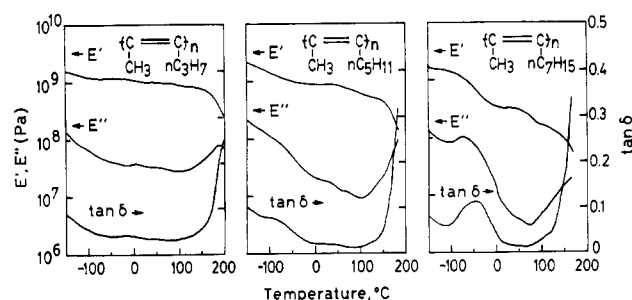


Figure 7. Dynamic viscoelasticity of poly(2-alkynes) (-150 to +200 °C, 110 Hz).

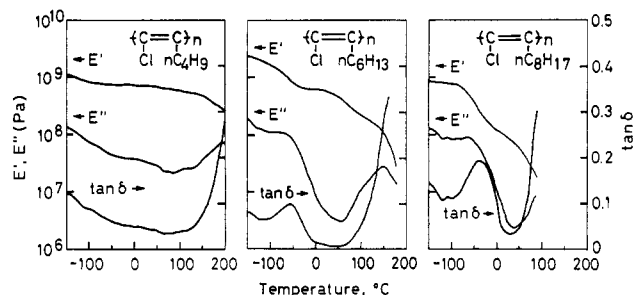


Figure 8. Dynamic viscoelasticity of poly(1-chloro-1-alkynes) (-150 to +200 °C, 110 Hz).

those of poly(2-decyne) and poly(1-chloro-1-decyne). This should stem from the fact that the silyl groups are more rigid than long linear alkyl groups.

Dynamic Viscoelasticity. Figure 6 illustrates temperature dependences of dynamic viscoelasticity for polymers of aromatic disubstituted acetylenes. In poly(1-phenyl-1-propyne), the variations of dynamic modulus (E'), dynamic loss (E''), and loss tangent ($\tan \delta \equiv E''/E'$) with temperature are quite small in the low-temperature region, indicating that the dispersion due to the rotation of methyl group is negligible. A decrease of E' and sharp increases of E'' and $\tan \delta$ are seen in the vicinity of 200 °C, being attributed to glass transition. The viscoelastic behavior of poly(1-chloro-2-phenylacetylene) is very similar to that of poly(1-phenyl-1-propyne).

In poly(1-phenyl-1-butyne), small changes in E'' and $\tan \delta$ are observed at low temperatures (Figure 6). For poly(1-phenyl-1-octyne), with a longer alkyl group, the changes become larger. The mechanical loss at low temperature in these polyacetylenes should result from the motion of the alkyl groups. Irrespective of the presence of long alkyl groups, the T_g 's of these polymers hardly differ from that of poly(1-phenyl-1-propyne).

Figure 7 shows the temperature dependence of the dynamic viscoelasticity for poly(2-alkynes). Poly(2-hexyne) shows changes in E' , E'' , and $\tan \delta$ around -150 °C, which should be dispersions due to the motion of methyl and *n*-propyl groups. The T_g of this polyacetylene is about 200 °C.

In poly(2-octyne) dispersions are seen at -80 °C owing to the motion of the *n*-pentyl group and in poly(2-decyne) at -50 °C owing to the motion of the *n*-heptyl group (Figure 7). Thus the dispersion shifts to higher temperature and the peak area of dispersion increases as the alkyl group of the poly(2-alkyne) becomes longer. The T_g of a poly(2-alkyne) decreases with increasing alkyl-group length: poly(2-octyne), 180 °C; poly(2-decyne), 160 °C. This contrasts with the result that the T_g of poly(1-phenyl-1-alkynes) is essentially independent of the length of alkyl groups.

Poly(1-chloro-1-alkynes) show viscoelastic behavior similar to that of poly(2-alkynes) (Figure 8). As the alkyl

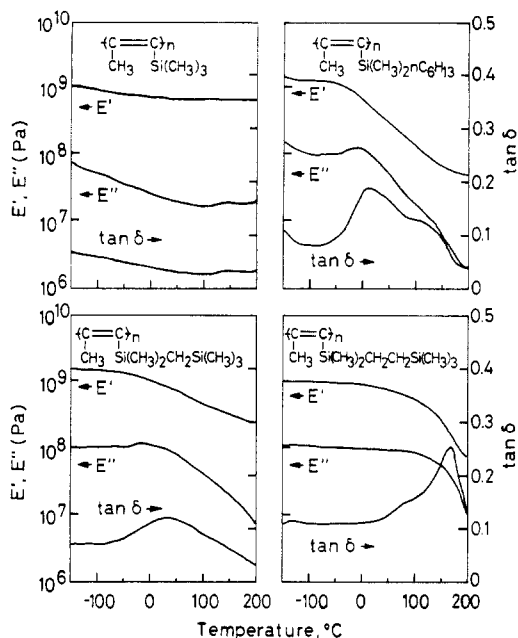


Figure 9. Dynamic viscoelasticity of poly(1-silyl-1-propynes) (−150 to +200 °C, 110 Hz).

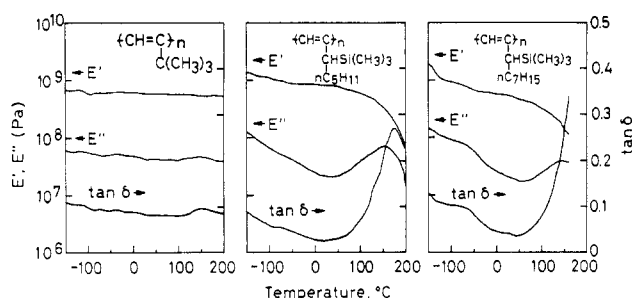


Figure 10. Dynamic viscoelasticity of monosubstituted acetylene polymers (−150 to +200 °C, 110 Hz).

group becomes longer (*n*-butyl to *n*-hexyl and *n*-octyl), the dispersion due to alkyl-group motion shifts to higher temperature (−100 to −60 to −40 °C) and the peak area of dispersion increases, while the T_g decreases significantly (190 to 150 to 90 °C). The effect of alkyl-group length on the T_g of poly(1-chloro-1-alkynes) is greater than that for poly(2-alkynes).

Figure 9 shows the temperature dependence of the dynamic viscoelasticity for polymers of Si-containing disubstituted acetylenes. Poly[1-(trimethylsilyl)-1-propyne] shows almost no changes in E' , E'' , or $\tan \delta$ in the range −150 to +200 °C. A very small peak of $\tan \delta$ at 150 °C might be due to the motion of the trimethylsilyl group. The T_g of this polymer is thought to be above 200 °C. The $\tan \delta$ of poly[1-(dimethyl-*n*-hexylsilyl)-1-propyne] shows peaks due to side-chain motions over a wide range of temperature. The T_g of this polymer should also be above 200 °C.

The polyacetylene with methyl and −Si(CH₃)₂CH₂Si(CH₃)₃ groups shows a dispersion around 50 °C, and its T_g is above 200 °C (Figure 9). The T_g of the polyacetylene with methyl and −Si(CH₃)₂CH₂CH₂Si(CH₃)₃ groups can also be above 200 °C; however, a possibility remains that its T_g is about 170 °C.

Among monosubstituted acetylene polymers, poly(*tert*-butylacetylene) shows virtually no dispersions in the range of −150 to +200 °C (Figure 10). A very small peak of $\tan \delta$ at 150 °C might be due to the motion of the

Table II
Glass Transition Temperatures, T_g 's, of Substituted Polyacetylenes

$-(CR_1=CR_2)_n-$		T_g , °C
R ₁	R ₂	
Ph	CH ₃	~200
Ph	C ₂ H ₅	~200
Ph	<i>n</i> -C ₆ H ₁₃	~200
Ph	Cl	~200
CH ₃	<i>n</i> -C ₃ H ₇	200
CH ₃	<i>n</i> -C ₅ H ₁₁	180
CH ₃	<i>n</i> -C ₇ H ₁₅	160
Cl	<i>n</i> -C ₄ H ₉	190
Cl	<i>n</i> -C ₆ H ₁₃	150
Cl	<i>n</i> -C ₈ H ₁₇	90
CH ₃	Si(CH ₃) ₃	>200
CH ₃	Si(CH ₃) ₂ - <i>n</i> -C ₆ H ₁₃	>200
CH ₃	Si(CH ₃) ₂ CH ₂ Si(CH ₃) ₃	>200
CH ₃	Si(CH ₃) ₂ CH ₂ CH ₂ Si(CH ₃) ₃	>200
H	C(CH ₃) ₃	>200
H	CHSi(CH ₃) ₃ - <i>n</i> -C ₅ H ₁₁	170
H	CHSi(CH ₃) ₃ - <i>n</i> -C ₇ H ₁₅	150

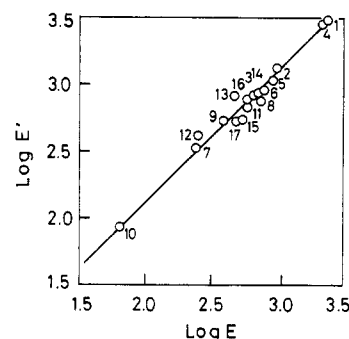


Figure 11. Logarithmic plot of Young's modulus, E , in the tensile test (25 °C, strain rate of 86% min^{−1}) against dynamic modulus, E' , in the dynamic mechanical measurement (25 °C, frequency of 110 Hz). The numbers in the figure refer to those in Table I.

tert-butyl group. The T_g of this polyacetylene must be above 200 °C. In poly[3-(trimethylsilyl)-1-octyne], a dispersion due to the *n*-pentyl group appears around −80 °C, and the T_g is 170 °C. As compared with this polyacetylene, poly[3-(trimethylsilyl)-1-decyne] has a peak of $\tan \delta$ at a higher temperature (−60 °C) owing to the motion of the *n*-heptyl group and T_g at a lower temperature (150 °C).

Table II shows T_g 's of substituted polyacetylenes from which the following conclusions can be reached: (i) the T_g 's of polyacetylenes with a phenyl group are about 200 °C irrespective of the other substituents; (ii) the T_g 's of polyacetylenes with bulky, rigid groups such as poly(*tert*-butylacetylene) and poly[1-(trimethylsilyl)-1-propyne] are above 200 °C; (iii) polyacetylenes with long alkyl groups like poly(2-decyne) and poly(1-chloro-1-decyne) have T_g 's below 200 °C; (iv) the effect of alkyl-group length on the reduction of T_g increases in the order $-(CPh=C-n-alkyl)_n- < -(CCH_3=C-n-alkyl)_n- < -(CCl=C-n-alkyl)_n-$, indicating that the effect becomes more prominent with decreasing bulkiness of the other group.

Discussion

Tensile and Dynamic Viscoelastic Properties. In general, the data on tensile properties are practically very useful, while those on dynamic viscoelasticity provide direct knowledge not only on modulus but also on mechanical damping. The tests complement each other.

Table III
Comparison of Glass Transition Temperatures, T_g 's, of Polyacetylenes with Those of Vinyl Polymers

$-(\text{CR}_1=\text{CR}_2)_n-$			$-(\text{CHR}_1\text{CHR}_2)_n-$		
R ₁	R ₂	T_g , °C	R ₁	R ₂	T_g , °C ^a
H	H	>150 ^b	H	H	-125
					(-21)
CH ₃	<i>n</i> -C ₃ H ₇	200	H	<i>n</i> -C ₃ H ₇	-40
H	C(CH ₃) ₃	>200	H	C(CH ₃) ₃	64
CH ₃	Ph	~200	H	Ph	100

^a Data from ref 22. ^b Data from ref 3.

Figure 11 shows the logarithmic plot of Young's modulus E , in the tensile test against dynamic modulus, E' , in the dynamic mechanical test, both measured at 25 °C. A least-squares treatment of this plot gives the equation $\log E' = \log E + 0.14$ (i.e., $E' = 1.4E$). This equation means that (i) E' is proportional to E , and (ii) E' is somewhat larger than E irrespective of the kind of polyacetylenes. Point (i) implies that the deformation levels in both tests were low enough to give the moduli in the linear viscoelastic region. Point (ii) seems to indicate that the deformation rate is higher in the dynamic mechanical test than in the tensile test.

In the tensile test polyacetylenes with long alkyl groups, except aromatic polyacetylenes, elongate appreciably [e.g., poly(2-decyne) and poly(1-chloro-1-decyne), see Table I]. Such polyacetylenes exhibit large dispersions below room temperature in the dynamic mechanical test (see Figures 7 and 8). Thus, there is an intimate correlation between the elongation at break and the dispersion below room temperature.

Comparison of Substituted Polyacetylenes with Polyacetylene. Young's modulus of *cis*-polyacetylene is no more than 200 MPa, and its elongation at break reaches 150–200%.^{1,2} These properties reflect the fact that *cis*-polyacetylene, which is prepared by Shirakawa's method, comprises fibrils with a sparse structure (density ~0.4 g/cm³). In contrast, *trans*-polyacetylene hardly elongates, being brittle. Owing to the difference in membrane structures, it is practically meaningless to compare the tensile properties of polyacetylene with those of substituted polyacetylenes.

The viscoelasticity of *cis*-polyacetylene hardly changes in the temperature range -100 to +150 °C; only small variations in E' and $\tan \delta$ due to *cis*-to-*trans* isomerization appear around 100 °C.³ Therefore, the T_g of polyacetylene should be above 150 °C, which corresponds to the present finding that the T_g 's of substituted polyacetylenes are as high as about 200 °C.

Comparison with Vinyl Polymers: Tensile Properties. Among vinyl polymers, aromatic polymers (e.g., polystyrene²⁰) are hard and brittle, whereas aliphatic polymers [e.g., poly(1-butene)²¹] are soft and ductile. Such substituent effects on tensile properties resemble those for substituted polyacetylenes revealed in the present study.

The presence of Cl, a polar substituent, makes vinyl polymers hard and brittle [e.g., $-(\text{CH}_2\text{CHCl})_n-$, $E \sim 3000$ MPa, $\gamma_B \sim 15\%$,²² $-(\text{CH}_2\text{CHCH}_3)_n-$, $E \sim 1300$ MPa, $\gamma_B \sim 700\%$ ²²]. In contrast, no such tendency was observed with substituted polyacetylenes [compare $-(\text{CCl}=\text{CPh})_n-$ with $-(\text{CCH}_3=\text{CPh})_n-$, and $-(\text{CCl}=\text{C-}n\text{-alkyl})_n-$ with $-(\text{CCH}_3=\text{C-}n\text{-alkyl})_n-$]. This result might be explained by the fact that the polar effect on Cl has been weakened by the conjugation of Cl with the double bond of main chain.

Comparison with Vinyl Polymers: T_g . Table III compares the T_g 's of several polyacetylenes with those of vinyl polymers having analogous structures.

The large difference in the T_g of polyacetylene (>150 °C) and that of polyethylene (-125 or -21 °C) is seemingly amazing. There are many factors controlling the T_g , such as the intermolecular interaction of polar substituents. However, the most important factor is probably the flexibility of the polymer chain; for example, the presence of an ether linkage reduces the T_g , whereas the introduction of a *p*-phenylene group increases it.²⁰ Therefore, the high T_g of polyacetylene is reasonable if it is considered that its main chain, comprising alternating double bonds, is quite stiff.

Since few vinyl polymers have two vicinal substituents in the repeat unit while many substituted polyacetylenes do, direct comparison of their T_g 's is difficult. However, vinyl polymers generally show low T_g 's that strongly depend on the kinds of substituents. This result probably reflects that the mobility of their main chains is principally governed by the nature (bulkiness, rigidity, polarity, etc.) of the substituents. On the other hand, the T_g 's of substituted polyacetylenes are about 200 °C, much higher than those of the corresponding vinyl polymers. Furthermore, the T_g 's of substituted polyacetylenes are not as affected by substituents as those of vinyl polymers (see Table III). It thus appears that the main factor in determining the T_g 's of substituted polyacetylenes is not the kind of substituents but the alternating double bond structure of the main chain.

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Registry No. (PhC≡CCH₃)_x, 53621-07-1; (PhC≡CC₂H₅)_x, 94844-29-8; (PhC≡CC₆H₁₃)_x, 98705-03-4; (PhC≡CCl)_x, 81953-16-4; (H₃CC≡CC₃H₇)_x, 42121-00-6; (H₃CC≡CC₅H₁₁)_x, 80652-33-1; (H₃CC≡CC₇H₁₅)_x, 80652-35-3; (ClC≡CC₆H₁₃)_x, 100858-76-2; (ClC≡CC₈H₁₇)_x, 100858-77-3; (ClC≡CC₁₀H₂₁)_x, 100858-79-5; (ClC≡CSi(CH₃)₃)_x, 87842-32-8; (H₃CC≡CSi(CH₃)₂C₆H₁₃)_x, 93094-72-5; (H₃CC≡CSi(CH₃)₂CH₂Si(CH₃)₃)_x, 99247-40-2; (H₃CC≡CCSi(CH₃)₂(CH₂)₂Si(CH₃)₃)_x, 100858-83-1; (HC≡CC(CH₃)₃)_x, 51730-68-8; (HC≡CCSi(CH₃)₂C₅H₁₁)_x, 100858-80-8; (HC≡CC(C₇H₁₅)Si(CH₃)₃)_x, 100858-82-0.

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Lignin. 22. Macromolecular Characteristics of Alkali Lignin from Western Hemlock Wood^{1a}

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ABSTRACT: Western hemlock wood platelets have been delignified with 1.0 N aqueous sodium hydroxide solution in a flow-through reactor. The extent of lignin removal was monitored by determination of the masses of residual lignin in the woody tissue (gel phase) and lignin fragments in the solution (sol phase). Increments of the reactor effluent were acidified to pH 2 to yield a series of acid-insoluble (AIL) and acid-soluble lignin (ASL) fractions. For the AIL, M_n and M_w values were obtained by vapor pressure osmometry and low-angle laser light scattering, respectively. For the ASL, the two molecular weight averages were estimated by size exclusion chromatography. Cumulative values of M_n and M_w for the sol-phase lignin were calculated and are interpreted in terms of previously proposed gel-sol transition concepts. The cross-links are found to be effectively tetrafunctional, and the cross-linking density appears to be about 0.07.

Introduction

The insolubility of native lignin gave rise to suggestions many years ago, for example, by Felicetta et al.² and by others,³ that lignins exist in wood as branched-chain polymer gels which can be made soluble, and delignification can be accomplished, only by hydrolysis or chemical cleavage of certain linkages within the polymer.

On the basis of application of the theory of Flory⁴ and Stockmayer⁵ (F-S theory), quantitative treatment of the depolymerization process was first approached by Szabo and Goring,⁶ who visualized a trifunctional polymerization proceeding in reverse to degrade a three-dimensional polymer gel. Gardner⁷ and K. V. Sarkanen studied the dissolution of a model network polymer ("Sephadex", a cross-linked dextran, supplied by Pharmacia of Sweden) by chemical degradation and found experimentally, different from the behavior of lignin and in accord with F-S expectations, that the rate accelerated as total dissolution was approached. Bolker and Brenner⁸ modified the Szabo-Goring model by introducing the concept of cross-linked "primary chains" of uniform length. Thereafter Yan and Johnson^{9,10} assigned a "most probable" size distribution to the primary chains and applied an extended version of the Stockmayer distribution.^{11,12} Glasser and Barnett,¹³ Gierer and Wannstrom,¹⁴ and others have called attention to the probable influence of lignin-hemicellulose and lignin-cellulose chemical bonds on the delignification process.

Pla¹⁵ measured the molecular weight distribution (MWD) of dioxane lignin and discussed his results in relation to the results of Bolker and Brenner⁸ and Bolker et al.¹⁶

As an alternative to these degelation concepts, another theory emphasizes physical effects.^{17,18} It is proposed that there is a relationship between pore size and the molecular weight of degraded lignin whereby the pores exert a sieving effect with the result that smaller lignin molecules diffuse early through the smaller pores, and large molecules dis-

solve only after the pores have been appropriately increased in size. This mechanism may significantly influence delignification, but it is difficult to quantify, as has been discussed in some detail by Yan.¹⁹

At present we find it preferable to work with the degelation concept based on the F-S theory, which is a chemical model and considers only the existence or non-existence of chemical bonds or linkages. In later studies it may become possible to add appropriate treatments to cope with some of the important chemical, geometric, and physical factors that must now be neglected, e.g., the possible linkages between lignins and some carbohydrates.

Several attempts have been made recently to characterize the polymeric structural changes of lignins during the course of delignification and degradation. These include the successive extraction of wood meal with dioxane-HCl²⁰ and the macromolecular characterization of the extracted lignin fractions,²¹ the incremental delignification with NaOH and kraft liquors with examination of probable condensation phenomena during pulping,^{22,23} and a theoretical interpretation based on the gel-sol transition with discussion of the effects of branching in lignin macromolecules.^{24,25}

We now briefly summarize the structural concepts to be used in the present work. In softwoods, it appears that the predominant guaiacyl structural units are linked mostly in a head-to-tail fashion to form "primary" chains, i.e., with a glyceryl side chain as the "head" in a structural unit and a phenolic hydroxyl grouping as the "tail". Thus the β -O-4 bond, which is the most abundant linkage in lignins, is such a head-to-tail bonding. In addition, each unit appears to have certain functional groups by which branching and cross-linking are possible. For example, both the α and 5 positions of a structural unit may be reactive and form cross-links. Thus, lignins and/or lignin-carbohydrate assemblies seem to exist in wood as three-dimensional polymers or gels that are insoluble in