Tensile and dynamic viscoelastic properties of various new substituted polyacetylenes

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The mechanical properties of aromatic and heteroatom-containing aliphatic polyacetylenes were examined. Regarding tensile properties, aromatic polyacetylenes [i.e. ring-substituted poly(phenylacetylene)s and poly(diphenylacetylene)s] showed large Young's moduli (500–2000 MPa) and small elongations at break (1–8%), implying that these polymers are hard and brittle. In contrast, Young's moduli of Si- and S-containing aliphatic polyacetylenes were rather small (several hundred megapascal), and their elongations at break were relatively large (several tens per cent); i.e. they are soft and ductile. This tendency was remarkable in the polymers having long *n*-alkyl chains. According to dynamic viscoelastic measurements, the glass transition temperatures (T_gs) of poly(diphenylacetylene)s were >200°C, whereas those of poly(phenylacetylene)s were 110–200°C, depending on the kinds of substitutents. The T_gs of aliphatic polyacetylenes are 40–160°C, lower than those of aromatic polyacetylenes. The effects of substituents on T_g are discussed in comparison with those of vinyl polymers.

(Keywords: substituted polyacetylene; tensile property; dynamic viscoelastic property)

INTRODUCTION

It has been found that group 5 and 6 transition-metal catalysts are effective for the polymerization of substituted acetylenes to afford polymers with high molecular weights (for a review, see ref. 1). The resulting polymers have alternating double bonds along the main chain, but assume more or less twisted conformations owing to the steric hindrance of the pendent groups. Consequently, polyacetylenes with bulky pendent groups show characteristics different from those of polyacetylene, e.g. solubility, various colours, air stability and electrical insulation. These characteristics are controllable by choice of substituents.

Previously we investigated the mechanical properties of various substituted polyacetylenes (mainly disubstituted acetylene polymers) to obtain the following results[2]: (i) polyacetylenes with phenyl groups are, in general, hard and brittle, while those with long alkyl chains are soft and ductile; (ii) the glass transition temperatures (T_gs) of most substituted polyacetylenes are around 200°C or higher and are hardly affected by the pendent groups. In other studies, the temperature dependence of dynamic modulus suggested the T_g of poly[1-(trimethylsilyl)-1-propyne] to be about 280°C (ref. 3), and effects of physical ageing on the viscoelasticity of the same polymer were examined[4].

In the present study, we investigated the tensile and dynamic viscoelastic properties of newly synthesized substituted polyacetylenes. The polymers examined are *ortho*-substituted poly(phenylacetylene)s [poly(PA)s], *para*- or *meta*-substituted poly(diphenylacetylene)s [poly(DPA)s], and aliphatic polyacetylenes containing an Si or S atom [i.e. poly(3-silyl-1-hexyne)s and poly(1-alkylthio-1-propyne)s]. The Young's modulus, tensile strength and elongation at break of the polymers were determined by tensile tests, and the T_gs by dynamic viscoelastic measurements. The results obtained, especially substituent effects on the mechanical properties, are discussed in comparison with those of conventional polymers.

EXPERIMENTAL

Synthesis of substituted polyacetylenes

For the synthesis of polymer samples, substituted acetylenes were polymerized according to the reported procedures. *Table 1* shows data on the synthesis and the relevant references. The catalysts employed are suitable Mo- and W-based catalysts for phenylacetylenes and 3-silyl-1-hexynes, $MoCl_5$–Ph_3SiH for 1-alkylthio-1-propynes, and $TaCl_5$–*n*-Bu_4Sn for diphenylacetylenes. Polymerization conditions were selected with reference to the literature shown in *Table 1* so that the polymer molecular weights could be as high as possible. Under such polymerization conditions, the polymer yields were >60%, and the weight-average molecular weights ($\bar{M}_w$) were 1.1×10^5–3.6×10^6.

Preparation of polymer membranes

Toluene solutions of polymers were cast on Petri dishes, and the solvent was slowly evaporated at ambient

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Table 1 Synthesis of substituted polyacetylene samples[a]

Sample no.	$\left(CR{=}CR'\right)_n$		Catalyst	Polymerization condition[b]	Yield (%)	$\bar{M}_w$[c] $\times 10^{-3}$	$\bar{M}_n$[c] $\times 10^{-3}$	Ref.
	R	R′						
1a	H	C_6H_4-*o*-$SiMe_3$	$MoCl_5$–Ph_3SiH	A	100	1900	500	10
1b	H	C_6H_4-*o*-CF_3	WCl_6–Ph_4Sn	A	100	690	190	11
1c	H	C_6H_4-*o*-$GeMe_3$	WCl_6	A	100	690	190	12
1d	H	C_6H_4-*o*-CH_2SiMe_3	$MoCl_5$–Ph_4Sn	A	96	700	450	13
1e	H	C_6H_2-*o*,*o*-Me_2-*p*-*t*-Bu	$W(CO)_6$–CCl_4–$h\nu$	B	100	2600	1400	14
1f	H	C_6F_4-*p*-*n*-Bu	WCl_6–Ph_3Sb	A	94	850	470	15
2a	Ph	C_6H_4-*p*-*n*-Bu	$TaCl_5$–*n*-Bu_4Sn	C	82	1300	460	16
2b	Ph	C_6H_4-*p*-*t*-Bu	$TaCl_5$–*n*-Bu_4Sn	C	84	3600	1400	16
2c	Ph	C_6H_4-*p*-$SiMe_3$	$TaCl_5$–*n*-Bu_4Sn	C	85	2200	750	17
2d	Ph	C_6H_4-*m*-$SiMe_3$	$TaCl_5$–*n*-Bu_4Sn	C	87	1400	250	17
2e	Ph	C_6H_4-*m*-$GeMe_3$	$TaCl_5$–*n*-Bu_4Sn	C	60	1800	730	18
2f	Ph	C_6H_4-*p*-OC_6H_5	$TaCl_5$–*n*-Bu_4Sn	C	69	1200	400	19
3a	H	$CH(SiMe_2$-*n*-$C_6H_{13})$–*n*-Pr	$MoCl_5$–Ph_3Sb	A	90	410	210	20
3b	H	$CH(SiMe_2Ph)$–*n*-Pr	WCl_6–Ph_3Sb	D	98	210	84	20
4a	Me	S–Et	$MoCl_5$–Ph_3SiH	C	58	130	35	21
4b	Me	S–*n*-C_6H_{13}	$MoCl_5$–Ph_3SiH	C	60	110	34	21
4c	Me	S–*n*-$C_{10}H_{21}$	$MoCl_5$–Ph_3SiH	C	78	170	39	21

[a] The polymers were synthesized according to the references listed in the last column

[b] A, Polymerized in toluene at 30°C for 24 h, $[M]_0 = 0.50$ M, [Cat] = [Cocat] = 20 mM. Part of the polymerization conditions were changed as follows; B, in CCl_4, [Cat] = 10 mM; C, at 80°C; D, at 0°C

[c] By g.p.c.

temperature for 1 week. The polymer membranes were further dried under a vacuum (0.1 mmHg) for 1 week to eliminate a trace of remaining solvent. The thickness of the polymer membranes was measured by a micrometer. The polymer membrane was homogeneous and uniform in thickness.

Tensile and dynamic viscoelastic tests

Tensile tests were carried out at 25°C at a strain rate of 86% min^{-1} on a 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 on a 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. The T_g was defined in this measurement as the temperature at which tan δ began to increase sharply.

RESULTS AND DISCUSSION

Tensile properties of substituted polyacetylenes

Figure 1 shows stress–strain curves for *ortho*-substituted poly(PA)s. All of the elongations at break for these polymers were less than 5%, irrespective of substituents. Their Young's moduli were 700–1000 MPa and were not affected by the substituents (*Table 2*). These findings indicate that *ortho*-substituted poly(PA)s are hard and brittle. The same tendency has been observed with β-substituted poly(PA)s such as poly(1-phenyl-1-propyne)[2].

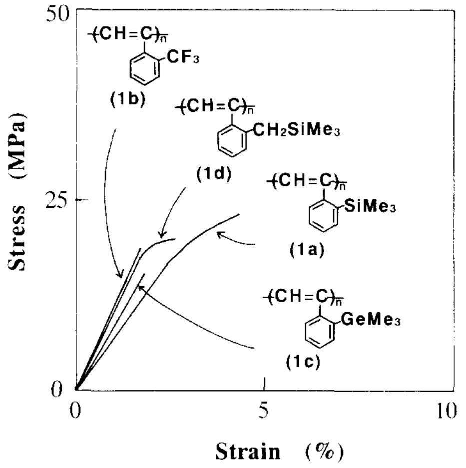

Figure 1 Stress–strain curves for *ortho*-substituted poly(PA)s (25°C, 86% min^{-1})

As can be seen in *Figure 2* and *Table 2*, poly(*p*-*t*-Bu-*o*,*o*-Me_2PA) (**1e**) and poly(*p*-*n*-Bu-*o*,*o*,*m*,*m*-F_4PA) (**1f**), which have many substituents on the phenyl ring, showed smaller Young's moduli (~500 MPa) and their elongation at break increased to 6–8%. These two polymers however, are also hard and brittle. These results lead to the conclusion that ring-substituted poly(PA)s are generally hard and brittle, although ring substituents have some influence.

Figure 3 shows stress–strain curves of poly(DPA)s having alkyl groups at the *para* position. The elongation at break for poly(*p*-*n*-BuDPA) (**2a**) was 6.6%, whereas that for poly(*p*-*t*-BuDPA) (**2b**) was 3.4%. This indicates that a polymer becomes more ductile as its substituent is more flexible, even though the carbon number is the same.

Poly(DPA)s containing heteroatoms (Si, Ge and O) are also hard and brittle, and show no yield points in the stress–strain curves (*Figure 4*). These observations are similar to those for ring-substituted poly(PA)s. Furthermore, the elongations at break of these polymers are slightly smaller than those of ring-substituted poly(PA)s. This is attributable to the introduction of one or two more phenyl groups in the polymer unit. Despite the same substituent ($SiMe_3$), the Young's modulus of poly(p-Me_3SiDPA) (**2c**) is almost twice that of poly(m-Me_3SiDPA) (**2d**), which suggests that the *para* substituents make the polymer harder than the *meta* groups.

Stress–strain curves of Si-containing poly(1-hexyne)s (**3a**, **3b**) are depicted in *Figure 5*. **3a**, which has a long alkyl group on the Si atom, shows a small Young's modulus of 210 MPa and a fairly large elongation at break of 65%. In contrast, having a rigid phenyl group on Si, **3b** exhibits a larger Young's modulus and a smaller elongation at break.

Tensile properties of polymers from S-containing aliphatic disubstituted acetylenes were examined (*Figure 6*). It is clear that, as the alkyl chain becomes longer from ethyl to n-hexyl and n-decyl groups, the Young's modulus (E) of the polymers decreases and the elongation at break (γ_B) tends to increase. When compared with poly(2-alkyne)s[2], the present S-containing polymers have larger Young's moduli and cannot be elongated so much; e.g.

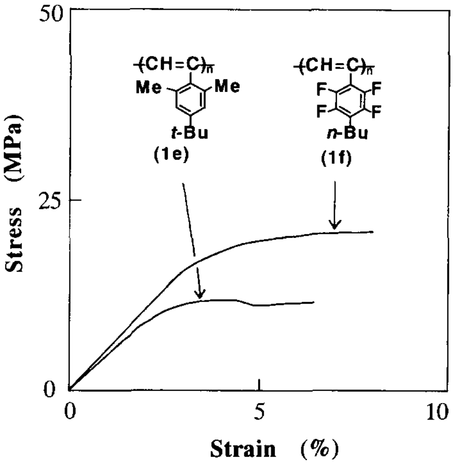

Figure 2 Stress–strain curves for poly(p-t-Bu-o,o-Me_2PA) and poly(p-n-Bu-o,o,m,m-F_4PA) (25°C, 86% min^{-1})

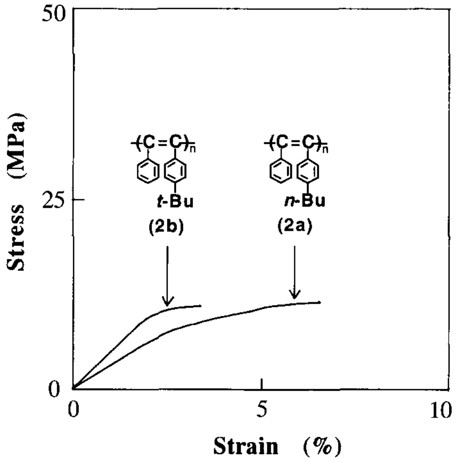

Figure 3 Stress–strain curves for *para*-substituted poly(DPA)s (25°C, 86% min^{-1})

Table 2 Tensile property data and glass transition temperature (T_g) of substituted polyacetylenes[a]

Sample no.	$-(CR{=}CR')_n-$		E[b] (MPa)	σ_B[c] (MPa)	γ_B[d] (%)	$\int_0^{\gamma_B} \sigma\, d\gamma$[e] ($MJ\ m^{-3}$)	T_g (°C)
	R	R′					
1a	H	C_6H_4-o-$SiMe_3$	700	23	4.3	0.6	190
1b	H	C_6H_4-o-CF_3	1100	18	1.7	0.2	130
1c	H	C_6H_4-o-$GeMe_3$	900	16	1.6	0.2	180
1d	H	C_6H_4-o-CH_2SiMe_3	1100	22	2.4	0.3	170
1e	H	C_6H_2-o,o-Me_2-p-t-Bu	510	11	6.4	0.7	>200
1f	H	C_6F_4-p-n-Bu	530	21	8.1	1.3	110
2a	Ph	C_6H_4-p-n-Bu	350	12	6.6	0.3	>200
2b	Ph	C_6H_4-p-t-Bu	800	11	3.4	0.1	>200
2c	Ph	C_6H_4-p-$SiMe_3$	1460	19	1.5	0.2	>200
2d	Ph	C_6H_4-m-$SiMe_3$	800	14	2.1	0.2	>200
2e	Ph	C_6H_4-m-$GeMe_3$	960	11	1.1	0.1	>200
2f	Ph	C_6H_4-p-OC_6H_5	2130	19	0.9	0.2	>200
3a	H	$CH(SiMe_2$-n-$C_6H_{13})$-n-Pr	210	6.1	65.0	3.7	40
3b	H	$CH(SiMe_2Ph)$-n-Pr	660	22	40.0	7.8	110
4a	Me	S-Et	1600	53	4.9	1.9	160
4b	Me	S-n-C_6H_{13}	340	18	20.0	3.2	110
4c	Me	S-n-$C_{10}H_{21}$	130	7.5	21.0	1.6	60

[a] Measured at 25°C and strain rate of 86% min^{-1}
[b] Young's modulus
[c] Tensile strength
[d] Elongation at break
[e] Energy to break (toughness)

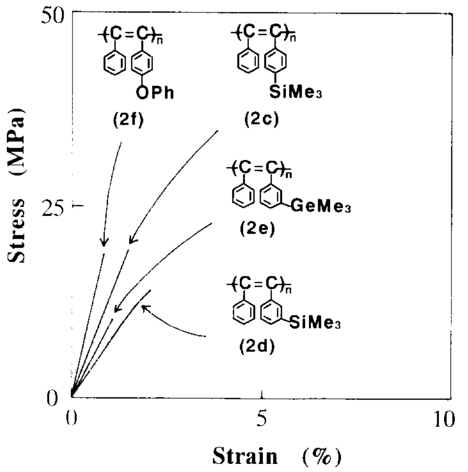

Figure 4 Stress–strain curves for poly(DPA)s containing heteroatoms (25°C, 86% min^{-1})

poly[1-(n-$C_6H_{13}S$)-1-propyne] (**4a**): $E = 340$ MPa, $\gamma_B = 20\%$; poly(2-decyne): $E = 260$ MPa, $\gamma_B = 180\%$). The polarity of sulfur may have rendered the S-containing polymers harder and less ductile.

The following points can be deduced from *Table 2*: (i) aromatic polyacetylenes generally show large Young's moduli and small values for the elongation at break and the energy to break, i.e. they are hard and brittle; (ii) no significant differences in tensile properties are seen between poly(PA)s and poly(DPA)s; (iii) the introduction of *n*-alkyl chain to the polymers (**1f**, **2a**) increases the elongation at break and the energy to break to a certain extent, toughening the polymers; (iv) aliphatic polyacetylenes, in general, possess yield points and show smaller Young's moduli, larger elongations at break and larger energies to break than do aromatic polyacetylenes. This tendency is remarkable for the polymers with long alkyl chains.

On the basis of the present and previous data^2, it can be said that, in general, Young's modulus decreases in the order of poly(DPA)s > poly(PhC≡CR) (R = *n*-alkyl, Cl) > poly(PA)s > poly(MeC≡CSR) (R = *n*-alkyl) ≃ poly(MeC≡CR) (R = *n*-alkyl) > poly(ClC≡CR) (R = *n*-alkyl). On the contrary, the elongation at break, γ_B, increases in this order.

The elongation at break for *cis*-polyacetylene reaches about 300%, while that for *trans*-polyacetylene is < 10% (ref. 5). This difference has not been examined clearly because it is associated with many factors such as crystallinity, morphology and fibril structure. The geometric structures of most substituted polyacetylenes are unfortunately unknown and hence their effects on mechanical properties are not clear. It is, however, evident that the kind of substituent has a large influence on the mechanical properties of substituted polyacetylenes.

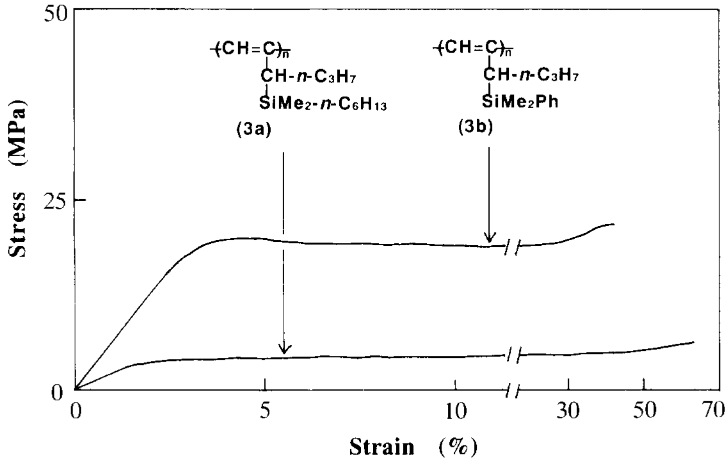

Figure 5 Stress–strain curves for poly(3-silyl-1-hexyne)s (25°C, 86% min^{-1})

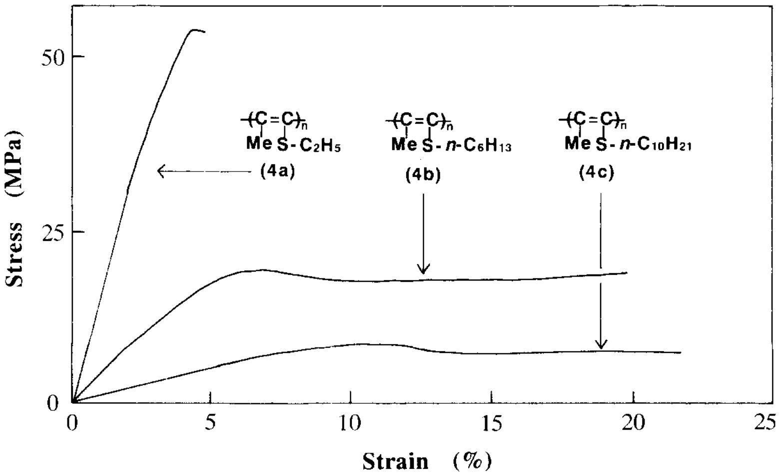

Figure 6 Stress–strain curves for poly(1-alkylthio-1-propyne)s (25°C, 86% min^{-1})

The following characteristics, which are generally seen with amorphous glassy polymers[6], also hold with the substituted polyacetylenes in this study. (1) The stress–strain behaviour for glassy polymers depends mainly upon intermolecular forces such as van der Waals' force, hydrogen bond, dipole–dipole interaction and so on. In other words, stress–strain behaviour is not greatly affected by the rigidity of the main chain. (2) The ductile nature (i.e. high elongation at break) appears in polymers having large dispersions due to secondary transitions, which suggests the inclusion of heterogeneous molecular aggregation (or different phases). The secondary transitions are brought about by introduction of substituents.

The following point should be emphasized: substituted polyacetylenes have a potential as high modulus and ductile non-crystalline polymers. In contrast, it is difficult to afford ductile characteristics to vinyl polymers in the glassy state. This is due to the fact that the introduction of substituents remarkably reduces the rigidity of the main chain.

Dynamic viscoelastic properties of substituted polyacetylenes

Figure 7 illustrates temperature dependences of dynamic viscoelasticity for *ortho*-substituted poly(PA)s. On the whole, the variations of dynamic modulus (E'), dynamic loss (E'') and loss tangent ($\tan\delta \equiv E''/E'$) are extremely small. The small peaks of E'' and $\tan\delta$ at low temperatures (<0°C) suggest dispersions due to the motion of *ortho* substituents. The $\tan\delta$ of poly(*o*-Me_3SiPA) (**1a**) begins to increase near 190°C, which indicates the onset of the glass transition. Poly(*o*-CF_3PA) (**1b**) shows a drastic increase in $\tan\delta$ at a lower temperature of 150°C. The T_g of poly(*o*-Me_3GePA) (**1c**), which consists of a structure similar to that of **1a**, is almost the same as that of **1a**. In poly(*o*-Me_3SiCH_2PA) (**1d**), which has a methylene group between the phenyl and silyl groups, the T_g is 170°C and lower than that of **1a**. Thus, the T_g values of *ortho*-substituted poly(PA)s are 200°C or slightly lower.

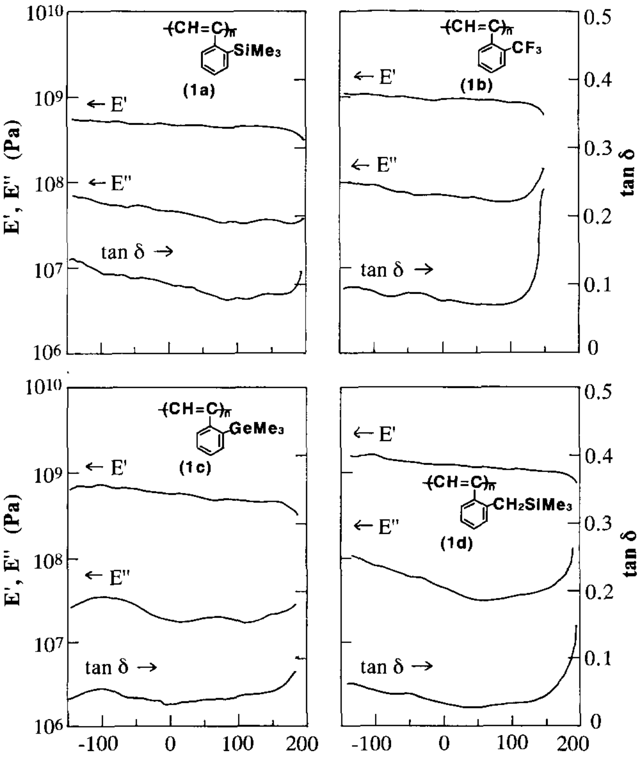

Figure 7 Dynamic viscoelasticity of *ortho*-substituted poly(PA)s (110 Hz)

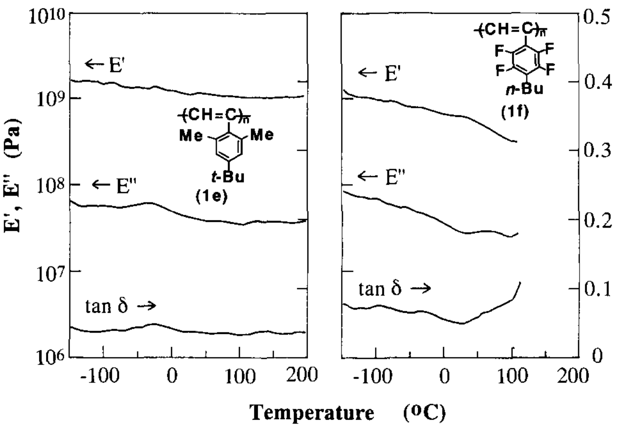

Figure 8 Dynamic viscoelasticity of poly(*p*-*t*-Bu-*o*,*o*-Me_2PA) and poly(*p*-*n*-Bu-*o*,*o*,*m*,*m*-F_4PA) (110 Hz)

Poly(*p*-*t*-Bu-*o*,*o*-Me_2PA) (**1e**) shows no significant changes in E', E'' and $\tan\delta$ between −150 and +200°C, except for a small dispersion around −30°C (*Figure 8*). In poly(*p*-*n*-Bu-*o*,*o*,*m*,*m*-F_4PA) (**1f**), the E' and E'' gradually decrease with increasing temperature and the T_g is rather low (110°C). The T_g values of polystyrene and poly(pentafluorostyrene) are 100 and 105°C, respectively[7], which suggests that the effect on T_g of fluorine atoms in the benzene ring is not large. Taking this into account, the low T_g of **1f** is explicable in terms of the presence of the *n*-Bu group rather than the presence of the fluorine atoms.

Figures 9 and *10* depict temperature dependences of viscoelasticity for poly(DPA) derivatives. None of these poly(DPA)s show a sharp increase of $\tan\delta$ below 200°C. Their T_gs are, therefore, higher than 200°C, in contrast to the case of poly(PA)s. In poly(*p*-*n*-BuDPA) (**2a**) and poly(*p*-*t*-BuDPA) (**2b**), no significant changes in E', E'' and $\tan\delta$ are seen over the temperature range of −150 and +200°C (*Figure 9*). Small dispersions at low temperatures in poly(*p*-Me_3SiDPA) (**2c**) and poly(*m*-Me_3SiDPA) (**2d**) might be attributable to the motion of Me_3Si groups (*Figure 10*). The viscoelastic behaviour of poly(*m*-Me_3GeDPA) (**2e**) scarcely shows temperature dependence in the range −150 to +200°C, while poly(*p*-PhODPA) (**2f**) shows a dispersion at −30°C, probably due to the motion of the phenoxy group.

The results of dynamic viscoelastic tests for Si-containing aliphatic polyacetylenes are shown in *Figure 11*. Polymer **3a**, which has a long alkyl chain on the Si atom, exhibits a large dispersion due to the motion of the hexyl group at −10°C and a sharp increase of $\tan\delta$ around 40°C corresponding to the glass transition. On the other hand, in polymer **3b**, which has rigid phenyl groups, there is no variation of E', E'' and $\tan\delta$ below 0°C, and its glass transition takes place at a temperature (140°C) higher than that of **3a**. Thus, it is apparent that a long alkyl group decreases the T_g of polymer more than the phenyl group.

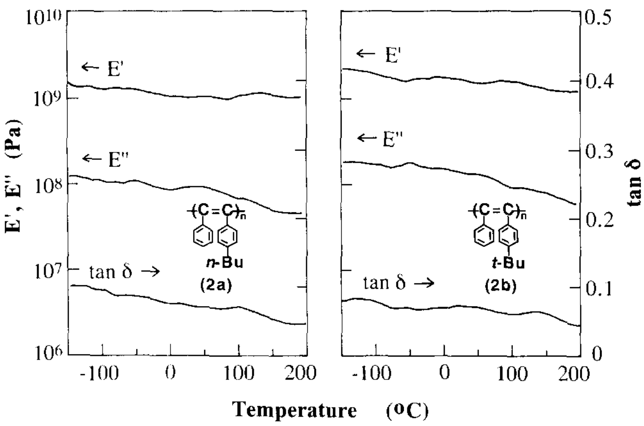

Figure 9 Dynamic viscoelasticity of *para*-substituted poly(DPA)s (110 Hz)

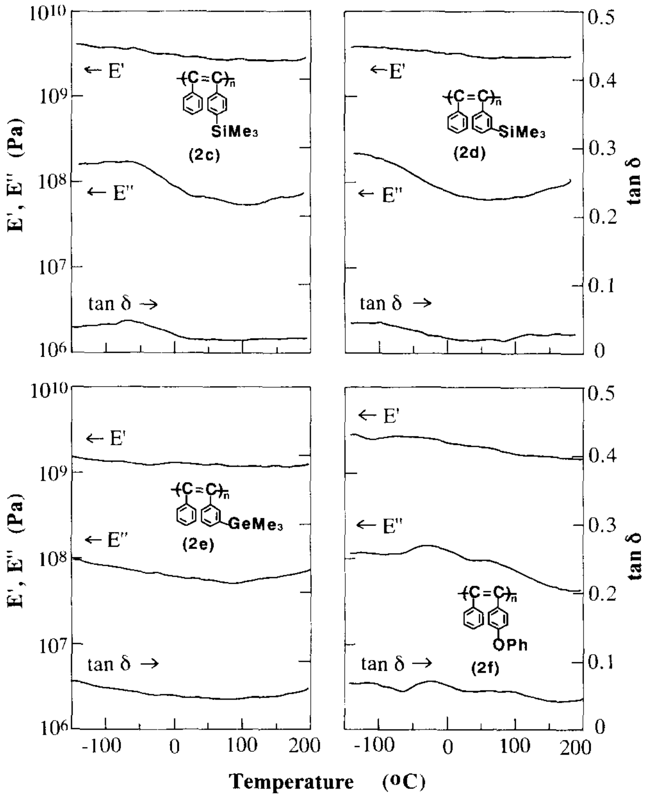

Figure 10 Dynamic viscoelasticity of poly(DPA)s containing hetero-atoms (110 Hz)

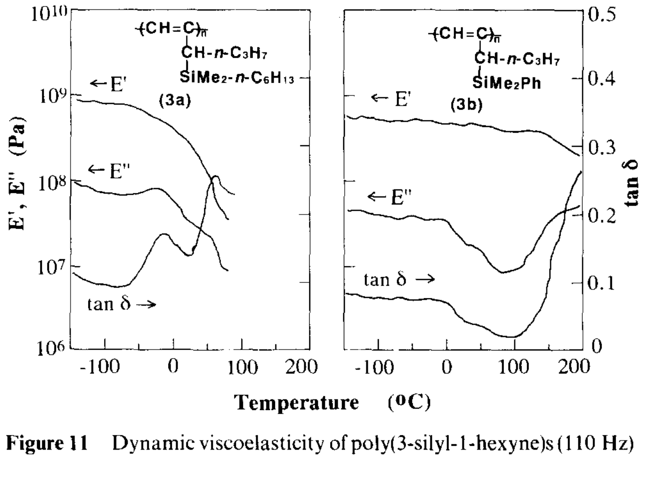

Figure 11 Dynamic viscoelasticity of poly(3-silyl-1-hexyne)s (110 Hz)

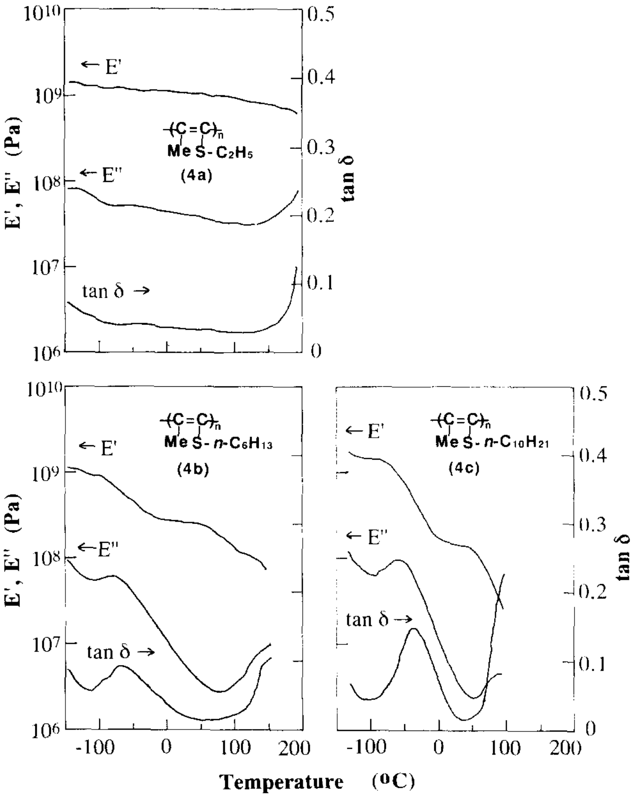

Figure 12 Dynamic viscoelasticity of poly(1-alkylthio-1-propyne)s (110 Hz)

Figure 12 shows the results of viscoelasticity for S-containing aliphatic polyacetylenes. It is obvious that, as the alkyl group becomes longer, the dispersion shifts to higher temperatures and the T_g decreases.

From the T_g values shown in *Table 2*, the following conclusions can be reached: (i) the T_gs of ring-substituted poly(PA)s are higher than 100°C and are considerably affected by the ring substituents; (ii) the T_gs of poly(DPA)s are higher than 200°C regardless of the position and type of ring substituents; (iii) the T_gs of Si- or S-containing aliphatic polyacetylenes are usually lower than those of aromatic polyacetylenes, which is obvious when the alkyl chain is long.

Taking the previous T_g data[2] into consideration, the T_gs of substituted polyacetylenes vary in the following order: poly(DPA)s > poly(PhC≡CR) (R = *n*-alkyl, Cl) > poly(PA)s ⩾ poly(MeC≡CR) (R = *n*-alkyl) ≃ poly(ClC≡CR) (R = *n*-alkyl) ≃ poly(MeC≡CSR) (R = *n*-alkyl). This clearly indicates that phenyl groups raise T_g and that long alkyl groups, on the contrary, lower T_g.

It is interesting to compare substituted polyacetylenes with vinyl polymers regarding the effect of substituents on T_g. The T_g of polymer is governed mainly by two factors, i.e. the nature of main chain and that of pendent groups.

The T_g of polyacetylene is > 150°C (refs 8, 9), while that of polyethylene is −125°C (ref. 7). This large difference no doubt originates from the difference in the main chain structures. When polyacetylenes are compared with polyethylenes having the same or similar substituents, the former polymers invariably inhibit higher T_g values, e.g. T_gs of polystyrene and poly(PA) are 100 and 120°C, respectively[7]. These reflect the higher rigidity of the main chain in the polyacetylene derivatives.

Regarding the effect of side groups on T_g, the rigidity and bulkiness of side groups greatly affect the T_g of vinyl polymers, e.g. the T_gs of polypropylene, polystyrene and poly(2,4,6-trimethylstyrene) are −10, 100 and 162°C, respectively[7]. This is because rigid and bulky groups of vinyl polymers strongly depress the mobility of the main chain, which is originally flexible. Though a similar effect of substituent is also seen in substituted polyacetylenes, the extent is much smaller. This is because the main chain of polyacetylenes is composed of alternating double bonds and hence essentially stiffer. In the polyacetylenes with long and flexible groups, on the other hand, phase conversion occurs, i.e. the side groups constitute a continuous phase and the main chains form a dispersed phase, which leads to considerable decreases in T_g. This effect is remarkable in substituted polyacetylenes, but less so in vinyl polymers which are originally flexible.

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