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Dynamic Mechanical Properties of Polypentenamers with Pendant Ionic Groups and their Hydrogenated Derivatives

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Dynamic mechanical properties of substituted polypentenamers having thioglycolate side groups and their hydrogenated derivatives have been studied. Methyl esters, acids and salts were investigated at two concentrations, 5.5 mole (%) and 9.2 mole (%). In the unhydrogenated derivatives, one principal relaxation, labelled β , exists in the temperature range from -160 to 100°C . This β relaxation arises from microbrownian segmental motion accompanying the glass transition. Its temperature is affected by the concentration of substituent but not the chemical nature of the substituent. A 'rubbery plateau' region exists in the acid and salt derivatives and in the latter the salt groups act as reinforcing fillers in this plateau region, consistent with the ionic domain model for their structures.

In the hydrogenated derivatives, three relaxations occur in the temperature range from -160 to 120°C and these are labelled α , β , and γ in order of decreasing temperature. The α relaxation arises from motions associated with the crystal phase except in the case of the 9.2 mole (%) sodium salt derivatives where it arises from motions occurring within ionic domains. The β relaxation arises from microbrownian segmental motions accompanying the glass transition, and the γ relaxation arises from localised motions which may involve both amorphous and crystalline phase components.

1. INTRODUCTION

The authors have previously reported on the preparation of polypentamer derivatives by thiol addition reactions resulting in the introduction of thioglycolate side groups along the polypentamer backbone.¹ It was shown that such derivatives can be prepared without backbone degradation and that the thioglycolate side groups can be obtained as esters, acids, or salts. In addition, the backbone can be hydrogenated to obtain a semicrystalline material. Depending upon the concentration and nature of the side groups and whether or not the backbone is hydrogenated, it is possible to obtain materials ranging from soft rubbers to tough plastics. In this paper are presented the results of a dynamic mechanical relaxation study of two series of substituted polypentenamers. These contain 5.5 mole (%) and 9.2 mole (%) of pendant groups and are designated PP-S(5) and PP-S(10) respectively. Within each series the properties of methyl esters, acids, and sodium salts are investigated. In this fashion it was hoped to compare properties for various derivatives which differed from one another only in the nature and concentration of the substituent and to determine the effect of backbone crystallinity on mechanical relaxation behaviour. It is well known that the introduction of side groups (which are capable of some form of interaction such as hydrogen bonding) into polymer chains has important effects on physical properties. Particularly striking is the effect of salt groups.^{2,3} In general when salt groups are introduced by the neutralisation of pendant acid groups, the tensile strength, impact resistance, and melt viscosity all undergo considerable enhancement. A model has recently been proposed to explain these phenomena which envisions the microphase separation of the salt groups into

ionic clusters or domains.⁴ The findings of this study are generally consistent with this model. Two factors exist, however, which tend to obscure the desired comparisons. First, a low level of crystallinity is present even in the unhydrogenated materials. This is due to the relatively large *trans* double bond content of the starting polypentamer (ca. 80%).⁵ Secondly it was found to be impossible to quantitatively convert the ester groups to free acid groups and the acid groups to salt groups. Nevertheless, it is possible to discern clearly the effects of the various substituents on the physical properties. The findings are generally in accord with previous results.³ The nature of the substituent, whether ester, acid or salt, affects the glass-rubber relaxation relatively little. The most striking effect is the modification of the pseudo plateau region which shows considerable enhancement in magnitude and persists to high temperatures in the case of the sodium salts. The hydrogenated derivatives exhibit behaviour which is quite similar to unsubstituted hydrogenated polypentamer. The principle effect of the substituents is to bring about a merging of the α and β relaxations. This is due to a decrease in the temperature of the α relaxation and an increase in that of the β relaxation. The quenched hydrogenated 9.2 mole (%) sodium salt derivative deviates from this behaviour inasmuch as it has a much lower crystalline content. In this derivative it is possible to observe a relaxation arising from motions within ionic domains.

2. EXPERIMENTAL

The starting polypentamer (PP) was kindly provided by the Goodyear Tire and Rubber Company. It contains 82% *trans* and 17% *cis* double bonds and has $M_N = 94000$ and $M_W = 172000$. Methyl thioglycolate was added to the double bonds by a free radical addition reaction previously described in detail.¹ Hydrogenation was accomplished utilising *p*-toluenesulphonyl hydrazide.⁶ The preparations of the derivatives are summarised by the following series of reactions.¹

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AIBN: azo bis isobutyronitrile

Reaction (1)

Reaction (2)

Reaction (3)

Acids and salts of the hydrogenated ester, HyPPS were prepared in a similar manner to the sequence represented in Reaction (3). Characterisation data for the samples investigated are collected in Table 1. It is to be noted that no evidence for backbone degradation was found for any of the derivatives.

Films suitable for dynamic mechanical testing were prepared by compression moulding at 150°C in the case of the PPS derivatives and at 180°C in the case of the HyPPS derivatives. Films were quenched by removing from the press and immediately immersing in a mixture of 'dry ice' and isopropyl alcohol. Annealing was carried out at 10° below the melting point for 24 hours followed by cooling to room temperature over a period of several hours.

Table 1. Characterisation Data for Substituted Polypentenamers

Sample	Pendant MTG Mole (%)	Degree of	
		Hydrolysis (%)	Neutralisation (%)
PPS(5)	5.5	—	—
PPS(5)H	—	90	—
PPS(5)Na	—	—	86
PPS(10)	9.2	—	—
PPS(10)H	—	78	—
PPS(10)Na	—	—	97
HyPPS(5)	5.5	—	—
HyPPS(5)H	—	84	—
HyPPS(5)Na	—	—	84
HyPPS(10)	9.2	—	—
HyPPS(10)H	—	72	—
HyPPS(10)Na	—	—	60

Dynamic Mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co., IMass, Inc.). The temperature range was from -160 to 130° and frequencies of 3.5, 11 and 110 Hz were used. Samples were heated at 1-2°/min under dry nitrogen.

Differential Scanning Calorimetry (DSC) measurements were carried out on a Perkin-Elmer Instrument, Model DSC II. The scanning speed was 10°C/min in all cases and indium was used as a calibration standard. The peak temperature of the melting endotherm was taken to be the melting point of the polymers.

3. RESULTS AND DISCUSSION

In general, in the PPS derivatives, one major relaxation occurs which is identified with microbrownian segmental motion accompanying the glass transition. In addition to this it is possible to discern a small sub T_g relaxation, labelled γ , in some of these derivatives, and a higher temperature process associated with melting. This latter is only discernible in a few cases, particularly in the PPS(5) series and is most clearly evident in the decrease of E' accompanying it. Fig.1(a), (b), and (c) shows the temperature dependences of E' and E'' at 110 Hz for PPS(5), PPS(5)H and PPS(5)Na, and the phenomena discussed above are identified in the figure. Both PPS(5) and PPS(5)H exhibit 'melting' processes while PPS(5)Na does not show any clearly defined feature associated with melting. Particularly remarkable is the extent of the plateau region in PPS(5)Na. Fig.2(a), (b), and (c) shows the temperature dependences of E' and E'' at 110 Hz for PPS(10), PPS(10)H and PPS(10)Na. In this case the melting process is not discernible except in the case of PPS(10). Otherwise the same features are evident as in the PPS(5) derivatives. Table 2 collects the relaxation data for the 6 polymers depicted in Figs 1 and 2 together with T_g 's measured by DSC. It is to be noted that both the calorimetrically determined T_g 's and the β relaxation associated with them are relatively insensitive to the nature of the substituent, whether it be ester, acid, or salt. The small secondary relaxation process, labelled γ , which is rather ill defined, exhibits no discernible dependence on either the concentration or nature of the substituent. It was previously suggested that the γ process in the amorphous polypentenamer involves local motions of the three methylene groups between the double bonds.⁷ It is possible that the same mechanism accounts for the γ relaxation in the substituted polypentenamers.

The extended 'rubbery plateau' region in PPS(5)Na and PPS(10)Na indicates that these materials act like crosslinked rubbers, at least at short times. This is indeed the case, although it is possible to mould the materials very satisfactorily at temperatures of 150°. It is clear that the plateau moduli shown in Figs 1 and 2 are far from equilibrium values, but relative comparisons may be made among the various substituents. Elementary rubber elasticity theory predicts the equilibrium modulus⁹ of a tetrafunctionally crosslinked elastomer to be

$$E = \frac{3\rho}{M_c} RT \quad (1)$$

E : Plateau modulus (Young's modulus)

ρ : density

Fig.1 (a) Temperature dependences of E' and E'' at 110 Hz for PPS(5).

(b) Temperature dependences of E' and E'' at 110 Hz for PPS(5)H.

(c) Temperature dependences of E' and E'' at 110 Hz for PPS(5)Na.

● E' ○ E''

Fig.2 (a) Temperature dependences of E' and E'' at 110 Hz for PPS(10).

(b) Temperature dependences of E' and E'' at 110 Hz for PPS(10)H.

(c) Temperature dependences of E' and E'' at 110 Hz for PPS(10)Na.

● E' ○ E''

Table 2. Temperatures of Transitions and Relaxations in Substituted PP's (°C at 110 Hz)

Sample	T_g^a	T_m^b	$\gamma(E'')$	$\beta(E'')$	"Melting" ^c	$\gamma(\tan\delta)$	$\beta(\tan\delta)$
PP	-98	10	—	-85	10	—	-70
PPS(5)	-94	—	-135	-74	0	—	-65
PPS(5)H	-92	—	-119	-78	-10	—	-70
PPS(5)Na	-91	—	-120	-84	—	-120	-71
PPS(10)	-89	—	-117	-77	-20	—	-68
PPS(10)H	-87	—	-112	-71	—	—	-57
PPS(10)Na	-87	—	-118	-76	—	—	-56

a Determined by DSC (Ref. 1)

b Reference 6

c Taken as the midpoint in the E' transition

R : gas constant
T : absolute temperature
 M_c : molecular weight of a network chain

Assuming that the substituents act as tetrafunctional cross-links, we obtain $M_c \approx 1200 \text{ g mole}^{-1}$ for the PPS(5) series and $M_c \approx 730 \text{ g mole}^{-1}$ for the PPS(10) series. Those values translate into equilibrium moduli of $6 \times 10^7 \text{ dynes cm}^{-2}$ for

Fig.3 (a) Temperature dependences of E' and E'' at 110 Hz for HyPPS(5).
(b) Temperature dependences of E' and E'' at 110 Hz for HyPPS(5)H.
(c) Temperature dependences of E' and E'' at 110 Hz for HyPPS(5)Na.
• E' ○ E''

Fig.4 (a) Temperature dependences of E' and E'' at 110 Hz for HyPPS(10).
(b) Temperature dependences of E' and E'' at 110 Hz for HyPPS(10)H.
(c) Temperature dependences of E' and E'' at 110 Hz for HyPPS(10)Na.
• E' ○ E''

Table 3. Temperatures of Transitions and Relaxations in Annealed Substituted HyPPS ($^{\circ}\text{C}$ at 110 Hz)

Sample	T_m^a	W_c^a	$\gamma(E'')$	$\beta(E'')$	$\alpha(E'')$	$\gamma(\tan\delta)$	$\beta(\tan\delta)$	$\alpha(\tan\delta)$
HyPP	130	85	-115	-3	80	-112	10	100
HyPPS(5)	118	80	-113	-6	70	-108	8	71
HyPPS(5)H	119	80	-112	20	90	-109	48	100
HyPPS(5)Na	120	80	-111	40	90	-109	-12	94
HyPPS(10)	109	75	-110	-13	45	-105	8	33
HyPPS(10)H	110	75	-114	20	63	-101	44	64
HyPPS(10)Na	112	75	-112	16	59	-111	40	58

a Determined by DSC (Ref. 6)
(W_c = weight percent crystallinity)

the PPS(5) series and 1×10^8 for the PPS(10) series at 300 K. It is known that carboxylic acids at small concentrations present as side groups in non polar polymeric chains are completely dimerised and are thus equivalent to crosslinking points, albeit labile ones.⁸ Unfortunately, reliable measurements in the plateau region are not available for the PPS(5)H polymer but the PPS(10)H polymer has a plateau value of E' of 2.0×10^7 dynes cm^{-2} in the vicinity of 300 K at 110 Hz. The value calculated from Equation (1) is high since not all the substituents have been hydrolysed to form the acid. Even if allowance is made for this, a value of E for PPS(10)H of about 8×10^7 is obtained from Equation (1), larger than the measured value by a factor of 4. Since Equation (1) would be expected to provide an underestimate of the true value, neglecting, as it does, such factors as chain entanglements and network imperfections, and since the measured value of E' would be expected to be an overestimate of the true value, it appears that hydrogen bonding is not very effective as a crosslinking agent.

The value of E' for PPS(10)Na, by contrast, is 2.5×10^8 , at 300 K. The neutralisation process, rather than merely replacing one type of crosslink with another, appears to have introduced reinforcement into the material as well.

The Guth-Einstein-Smallwood equation is

$$\frac{E_f}{E_o} = 1 + 2.5 v_f + 14.1 v_f^2 \quad (2)$$

E_f : equilibrium modulus of filled elastomer

E_o : equilibrium modulus of unfilled elastomer

v_f : volume fraction filler

This relationship purports to describe the modulus enhancement as a function of volume fraction filler. It has been shown to be valid for various reinforcing fillers in elastomers up to values of v_f of about 0.3.⁹ At $v_f = 0.3$, Equation (2) predicts a value of $E_f/E_o \approx 3$. The value of the ratio of E' for PPS(10)Na to that for PPS(10)H is about 12. This dramatic effect is most easily explained on the basis of domain formation in the sodium salt. The ionic clusters act as a combination of multifunctional crosslinks and as very efficient reinforcing fillers.

The hydrogenated derivatives show very different relaxation behaviour from the unsaturated materials. Complete hydrogenation of the parent PP leads to a material resembling linear polyethylene, with a melting point of 130°C and a crystallinity of 85%.⁷ Three relaxation regions occur in HyPP below the melting point and these are labelled α , β , and γ in order of decreasing temperature. The α relaxation depends on morphology and is at least in part associated with the crystal phase. The β relaxation arises from micro-brownian segmental motions accompanying the glass transition and the γ relaxation is a composite secondary dispersion involving reorientation of a few CH_2 units in the amorphous phase and a local crystal phase motion. Fig.3(a), (b), and (c) illustrates the temperature dependences of E' and E'' at 110 Hz for annealed HyPPS(5), HyPPS(5)H and HyPPS(5)Na, while Fig.4(a), (b), and (c) illustrates the temperature dependences of E' and E'' at 110 Hz for annealed HyPPS(10), HyPPS(10)H, and HyPPS(10)Na. Table 3 collects relevant relaxation data for all the polymers studied. Inasmuch as the α relaxation is not very prominent in the E'' plots, the $\tan \delta$ values are more reliable (Figs 5 and 6). The overall effect of the substituents in the HyPP's is to cause a merging of the α and β processes. In the first place

Fig.5 (a) Temperature dependence of $\tan \delta$ at 110 Hz for HyPPS(5).
(b) Temperature dependence of $\tan \delta$ at 110 Hz for HyPPS(5)H.
(c) Temperature dependence of $\tan \delta$ at 110 Hz for HyPPS(5)Na.

the α relaxation temperature decreases because the substituents lower the degree of crystallinity. The β relaxation temperature increases on the other hand because the substituents tend to raise T_g . Relatively little change occurs in the γ relaxation either in magnitude or temperature among the various substituents. It is also to be noted that although the substituent concentration affects the degree of crystallinity, the nature of the substituent has essentially no effect in these well annealed samples.

Table 4 collects relaxation data for the quenched HyPPS(10) series. Quenching has little effect on the degree of crystallinity of the ester derivative, but reduces the crystallinity of the sodium salt by nearly a factor of 2. In the case of HyPPS(10)H, no α relaxation is discernible, while that of HyPPS(10) is considerably reduced in magnitude. The be-

Table 4. Temperatures of Transitions and Relaxations in Quenched Substituted HyPPS(10) (°C at 110 Hz)

Sample	W_c^a	$\gamma(E'')$	$\beta(E'')$	$\alpha(E'')$	$\gamma(\tan\delta)$	$\beta(\tan\delta)$	$\alpha(\tan\delta)$
HyPPS(10)	75	-113	-11	34	-106	10	40
HyPPS(10)H	70	-111	16	—	-107	40	—
HyPPS(10)Na	40	-106	15	61	-100	32	62

a Weight fraction crystallinity by DSC

haviour of the quenched HyPPS(10)Na is curious. Although it has much lower crystallinity than either HyPPS(10) or HyPPS(10)H, it has a larger α relaxation occurring at a higher temperature than the α relaxation of annealed HyPPS(10)Na. It has previously been suggested^{11,12} that a relaxation occurs in ionomers which reflects motions in ionic clusters or domains, and, in the case of monovalent salts, this relaxation is located in the temperature range 50–100°C. It is therefore likely that the α relaxation in quenched HyPPS(10)Na, (and possibly in annealed HyPPS(10)Na as well, although the results are obscured by the high crystallinity of this polymer), arises from motions within ionic domains.

While the substituents have a noticeable effect on the dynamic mechanical properties of the hydrogenated derivatives studied, their properties are determined to a large extent by crystallinity. Thus, in all cases the β relaxation has undergone a considerable increase in temperature in the HyPPS derivatives compared to the PPS derivatives just as was previously observed with HyPP compared to PP. Values of E' show some differences in the α and β relaxation regions depending on the degree to which these two dispersions are merged in the different derivatives.

4. CONCLUSIONS

The relaxation process accompanying the glass transition (β process) in the PPS derivatives is affected by the substituent concentration but not by the substituent nature (i.e., whether the substituent is an ester, acid, or salt). The crystallinity present in the HyPP derivatives has a much greater effect on the β relaxation than the substituents.

In the 'rubbery plateau' region, the salt groups of the PPSNa derivatives act as reinforcing fillers. This is consistent with the hypothesis that they are clustered to form ionic domains.

The α relaxation in the HyPPS derivatives is dependent on degree of crystallinity and morphology both in temperature and in magnitude.

The α relaxation in the HyPPS(10)Na derivative arises from motions within ionic domains.

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Fig.6 (a) Temperature dependence of $\tan \delta$ at 110 Hz for HyPPS(10).
(b) Temperature dependence of $\tan \delta$ at 110 Hz for HyPPS(10)H.
(c) Temperature dependence of $\tan \delta$ at 110 Hz for HyPPS(10)Na.

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