July, 1990] © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***63***, *2089—2093 (1990)*

Synthesis of Dimethylamino Terminated Poly(tetrahydrofuran) and Adhesion Property of Poly(tetrahydrofuran) Ionene Prepared Therefrom

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(Received February 15, 1990)

In order to establish the polymerization conditions for the synthesis of bifunctional dimethylamino group terminated poly(oxytetramethylene) (AT-PT), living cationic polymerization of tetrahydrofuran by trifluoromethanesulfonic anhydride was carried out. Especially, factors determining the molecular weight were investigated. The polymerization enabled us to prepare monodispersed AT-PTs having molecular weght between 2000 and 10000. The resultant AT-PTs were bifunctional, i.e., each molecule contains two dimethylamino groups. From AT-PT and dihalide, poly(oxytetramethylene) ionene (PTI) was synthesized in a thin film form. Tensile properties of the PTI films revealed that the films were very tough and elastic. PTI was also found to have high peel strength towards the Bakelite surface. The peel strength increased with the increase of cationic site on PTI main chains, i. e., with the decrease of molecular weight of AT-PT. PTI also had a high permeability of moisture due to the presence of ionic sites. From these results, PTI can be a promising adhesive material for some biomedical application.

Polymers having functional groups at their chain ends are known as telechelic polymers, or often as a telechelic oligomer when the molecular weight is relatively low. They are very useful materials for the preparation of a functionalized polymeric material including adhesives for special purposes.1) Among these oligomers, polyether polyols are of much use in order to synthesize polyurethanes in combination with di- or triisocyanate.2)

Poly(oxytetramethylene) glycol (PTMG) is especially important, because PTMG based polyurethanes show excellent mechanical properties, such as very good tensile properties and perhaps the highest antifatigue property among elastomers.3,4) Additionally, PTMG-based polyurethanes are known to be biocompatible,5—7) thus used in the fabrications of artificial hearts.8) However, there appeared few reports on the synthesis of poly(oxytetramethylene) having functional groups other than hydroxyl group.9)

In this report a synthetic route of dimethylamino group terminated poly(oxyethylene) (AT-PT) is established, followed by the reaction with dihalide to give ionene-type poly(oxytetramethylene) (PTI).10,11) PTI is found to show excellent tensile properties like PTMG-based polyurethanes.11) We have also recognized the adherence of PTI onto human skin. AT-PTs with various molecular weights are synthesized, and the PTIs from them are subject to tensile and peeling tests in order to explore possibility of PTI as an adhesive, for example, for biomedical uses.

Experimental

Materials. AT-PT was synthesized by cationic ring-opening polymerization of tetrahydrofuran (THF). THF was purified by distillation several times on sodium wire until a blue color appearance by benzophenone. Trifluoromethanesulfuric anhydride, which is used as an initiator of cationic polymerization, was prepared according to Burden et al.12) Dimethylamine was freed from moisture by passing through a column packed with KOH pellets just before use. The reaction conditions of cationic polymerizations are shown in Table 1. The polymerization was conducted in an ice bath (2 °C) or at 25 °C under a dry nitrogen stream. It was essential to minimize the influence of adventitious water to prepare telechelic, AT-PTs.

AT-PT was reacted with α,α'-dichloro-*p*-xylene to give PTI.10,11) At first the reaction was carried out in THF at 30 °C for one hour, and the reaction mixture was poured onto a Teflon® mold. After the evaporation of THF the mold was kept at 100 °C for two hours under a gentle stream of dry nitrogen gas.

Analyses of AT-PT and PTI. The reaction products were analyzed by a few techniques. The dimethylamino group content in AT-PT was assayed by non-aqueous titration with perchloric acid in acetic acid solution. Infrared spectra were obtained on a Hitachi 215 IR Spectrometer. Proton NMR was recorded on a Varian T-60 A Spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard.

Tensile Property Measurents. Tensile stress-strain curves were obtained on a tensile tester TOM 200D at room temperature. The crosshead speed was 10 mm min^{-1}. The measurements were carried out on dumbell-shaped specimens (JIS No. 3) at least three times and the average value was used.

Peeling Tests. As adherends three plates were used. A Bakelite plate and a glass plate were used after the surface cleaning by acetone. The surface of a stainless steel plate (SUS 304-27CP) was treated according to JIS R6253. The preparation of test sample was as follows: Ethanol solution of PTI (ca. 30%) was applied on the surface of adherend (the area=4×5 cm^2 and the amount of PTI=0.015—0.020 g cm^{-3}). After 5 min standing, a cotton canvas sheet(No. 10) was placed on PTI layer on the adherend and pressed. The test

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Table 1. Polymerization of THF by $(CF_3SO_2)_2O$

No.	[I]	Temp	Time	[Amine]	Conv.	MW	M_w	[DAG]	Functionality	
	mol l^{-1}	°C	min	[I]	%		M_n	×10^4 mol l^{-1}	Titration	NMR
1	0.078	25	5	147	10.2	2920	1.16	6.30	1.84	1.9
2	0.117	25	5	73	32.6	3800	1.21	5.20	1.98	—
3	0.156	25	5	73	46.4	4400	1.27	4.55	2.00	—
4	0.240	25	5	73	53.4	3050	1.65	5.56	1.79	1.8
5	0.300	25	5	73	54.8	3150	1.61	5.78	1.82	1.8
6	0.078	2	10	73	13.8	2170	1.18	8.17	1.77	1.9
7	0.078	2	15	73	15.1	3460	1.14	5.72	1.98	—
8	0.078	2	25	73	30.8	6290	1.19	2.99	1.88	—
9	0.078	2	25	73	43.3	9740	1.17	2.01	1.95	—
10	0.130	2	10	45	31.3	3270	1.19	5.85	1.91	1.9
11	0.259	2	10	73	60.7	8740	2.33	2.26	1.97	—

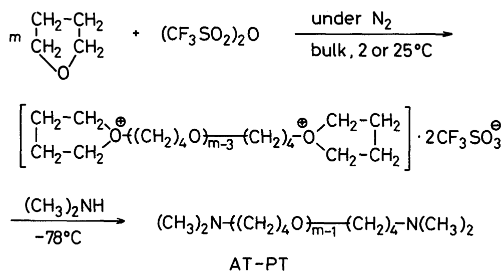
I=$(CF_3SO_2)_2O$, initiator. Amine=dimethylamine. Conv. is relative to the initial THF feed. MW=molecular weight by VPO. M_w/M_n=weight-average over number-average molecular weight by GPC. DAG is dimethylamino group in AT-PT. Functionality=number of dimethylamino group per polymer.

sample was dried under vacuum at room temperature. The 180°-peeling tests were conducted at room temperature. The measurements were repeated untill five stable stress-strain curves were obtained.

Gas-Permeability Measurements. Permeability of PTI film was measured by the standard method which is very similar to ASTM D 1434-75 when penetrant was nitrogen or oxygen. Moisture permeability was determined by so called "cup" method (JIS Z 0208).[13]

Results and Discussion

Synthesis of AT-PT. Synthetic route of AT-PT from THF monomer is shown in Scheme 1. This synthesis is based on the report by Smith and Hubin[9] with a few modifications for the present product.[11] As they already reported, the amine compound had to be used in large excess to introduce the amino group onto the both poly(THF) chain ends (see Table 1). The reason why such an excess amine was necessary to get AT-PT is not fully elucidated yet. In considering this question, two factors have to be mentioned; the stability, in other words not much reactivity, of the tertiary oxonium cation from THF and the equilibrium nature of the THF polymerization. Due to these natures, it is necessary to use an excess of the end-blocking agent to ensure as rapid a termination reaction as possible. Otherwise, the functionality of AT-PT became much lower than 2.0 and the molecular-weight distribution was not monodispersed.



Scheme 1.

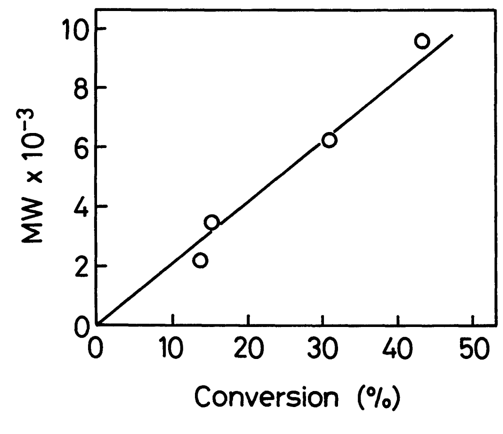


Fig. 1. Relationship between conversion and mol wt of AT-PT: Polymerization at 2 °C, [I]=0.078 mol l^{-1}.

Proton NMR of AT-PTs showed protons in *N*-methyl group at 2.2 ppm (singlet) which enabled us to evaluate the dimethylamino group contents in AT-PTs if their molecular weight were below ca. 3000, although the groups are only at the both ends of the polymeric chains. The assayed concentration of the group by proton NMR was in good agreement with that by titration. The polymerization conditions and the results are collected in Table 1. AT-PTs having the molecular weight between two and nine thousands were obtained, whose functionalities were very near to two. In other words, telechelic oligomers of poly(oxytetramethylene) were prepared.

Living nature of the present polymerization system is demonstrated in Fig. 1. With the progress of polymerization molecular weight increased linearly. This result and almost quantitative introduction of dimethylamino group to AT-PT strongly suggest the living nature of this cationic polymerization.

The molecular weights in Table 1 were measured on vapor pressure osmometer (VPO). However, it is much more convenient if they can be obtained by gel-permeation chromatography (GPC), calibrated by polystyrene standards. Figure 2 shows the relationship between VPO and GPC molecular weights of AT-PTs. The experimental results fit the following equation:

$$MW_{VPO} = 0.650 \times MW_{GPC} \qquad (1)$$

Equation (1) is in good agreement with that for poly(oxytetramethylene) reported by Burgess et al.[14]

Synthesis of PTI and Its Tensile Properties. AT-PT was reacted with α,α'-dichloro-*p*-xylene to form quaternary ammonium salt via the Menschutkin-type reaction as shown in Scheme 2. The kinetic study of this reaction was reported by us.[15] The synthetic process, which is described in Experimental section, affords PTI film directly from the mixture of starting materials. It is a kind of reactive processing, though the operational scale is very small.

The resulted films were highly elastomeric and very tough. Figure 3 shows a typical tensile stress-strain curve of PTI film. The stress remained very low until about 500% elongation, and further elongation brought abrupt increase of the stress to give a very high tensile strength with a very large elongation at break. The features appeared in Fig. 3 were observed on all the PTIs prepared here. The tensile modulus at 100% elongation, tensile strength, and elongation at break are listed in Table 2 in order to show the elastomeric nature of PTI for practical purposes. These tensile properties indicate that PTI is extremely flexible and has as high a strength as reinforced rubbers or polyether urethanes.

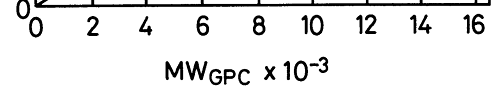
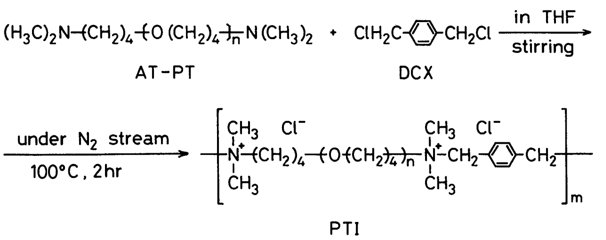


Fig. 2. Relationship between mol wt by GPC (calibrated by standard polystyrenes) and mol wt by VPO (number-average mol wt).



Scheme 2.

Adhesion Property of PTI. In the course of this study, we noticed that PTI did adhere to human skin very well. When methanol or ethanol solution of PTI was applied on the surface of human skin, very tough and flexible film was formed after evaporation of alcohol. Once the PTI films was formed, it was extremely difficult to remove the thin film from the skin. Sometime the only way was washing it out by alcohol. The adhesion property of PTI on human skin was to be investigated. However, it is difficult to conduct peeling test from human skin. As a substitute

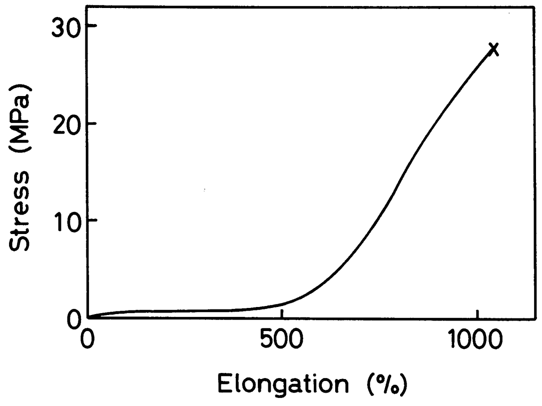


Fig. 3. Tensile stress-strain behavior of PTI (No. 3, mol wt of the precursor AT-PT was 4400).

Table 2. Tensile Properties of PTI

Sample code	MW of AT-PT	M_{100} MPa	T_b MPa	E_b %
6	2170	1.4	30.0	810
1	2920	1.5	28.0	730
4	3050	1.1	32.3	910
5	3150	1.5	32.0	770
10	3270	1.7	38.2	750
2	3800	1.6	39.6	710
3	4400	0.7	27.1	1110
8	6290	2.1	32.1	960
9	9740	5.5	32.2	880

M_{100}=tensile modulus at 100% elongation. T_b=tensile strength at break. E_b=elongation at break.

Table 3. 180° Peel Strength of PTI

Sample code	Peel strength/N m^{-1}		
	Bakelite	Stainless steel	Glass
6	1930	170	340
5	1610	70	40
8	1040	140	110
9	340	70	40

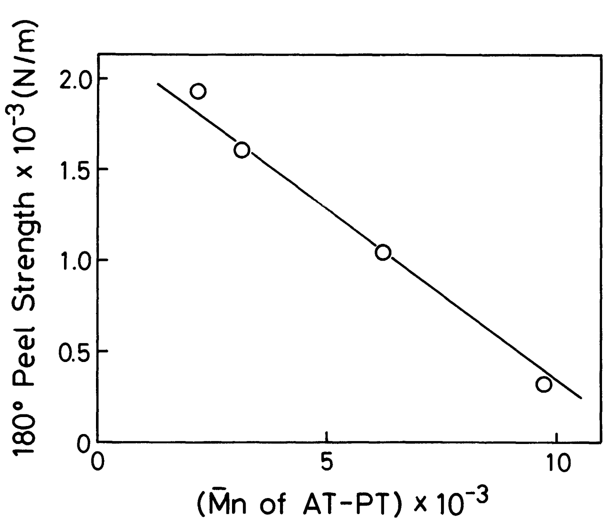


Fig. 4. Relationship between 180°-peel strength of PTI and mol wt of the precursor AT-PT. Adherend, the Bakelite surface.

of human skin, we chose a Bakelite surface and compared the results with those obtained on glass and metal surfaces.

Table 3 shows 180°-peel strength of PTI from Bakelite, stainless steel or glass surface. The results were the average of 5 times measurements. The peeling of PTI from the Bakelite sheet was found much more difficult than from the other two. Additionally, it seemed that the peel strength depended on the molecular weight of poly(oxytetramethylene) segment, i.e., the molecular weight of AT-PT. The relationship is displayed in Fig. 4. Very good linearity is recognized. In case of PTI, the smaller is the molecular weight of AT-PT, the more is the ionic site in a unit volume, hence the more polar it becomes. The results in Fig. 4 is explained by the number of ionic site, i.e., ammonium ion and its counter anion, which is one of the important factors determining the adherence.

There appeared a few theories relating peeling strength to Young's modulus. For example, Kaelble[16] proposed the following equation for 180 °peel:

$$P = \frac{a\ b}{4} \cdot \frac{\sigma_0^2}{E_a} \tag{2}$$

where a is thickness of adhesives, b width of adhesives, σ_0 tearing strength, E_a the Young modulus of adhesives. Also Fukuzawa[17] derived the following equation:

$$P = \frac{b\ t_a f_c^2}{4\ E_a} + \frac{b\ W_a}{2} \tag{3}$$

where t_a is thickness of adhesives, f_c inherent adhesive force of interface, E_a the Young modulus of adhesives, and W_a work for rupture to produce peeled surface. In accordance to these equations, the present peeling results of PTI from the Bakelite is related to the inverse of the Young modulus as shown in Fig. 5. Here the Young modulus was calculated from the initial slope of the tensile stress-strain curve. The number of experimental points is not enough to conclude, but we may say that modulus is one factor to influence adhesion of PTI. In case of PTI, the higher is the concentration of ionic sites, the higher are both the Young modulus and adhesiveness. Therefore it is quite natural that the relationship shown in Fig. 5 was observed.

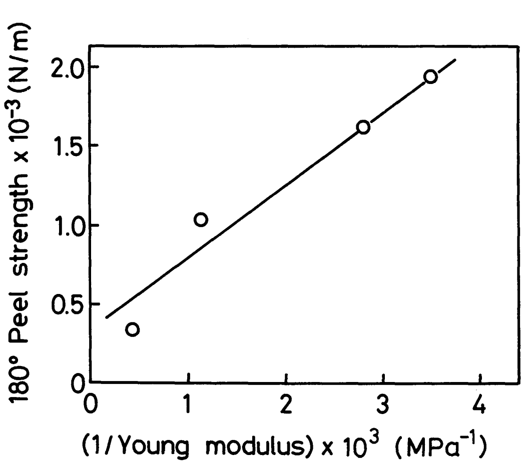


Fig. 5. Relationship between 180°-peel strength and the Young modulus of PTI. Adherend, the Bakelite surface.

Table 4. Gas Permeability of PTI

Sample	H_2O[a]	O_2[b]	N_2[b]
PTI	3.4	1.89	0.705
NR[c]	0.067	2.33	0.805

a) At 25 °C, in 10^9 g cm/cm^2 s cmHg (1 cmHg=1333.22 Pa). b) At 28 °C, in 10^9 cm^3 (STP) cm/cm^2 s cmHg. c) Natural rubber vulcanizate cured by sulfur.

Gas Permeability. When we think of adhesives for biomedical applications, gas permeability, especially that of moisture and of oxygen, are very important. The results on H_2O, O_2, and N_2 are shown in Table 4. Compared with natural rubber (NR) vulcanizate (sulfur cured), moisture permeability of PTI was much larger, while that of oxygen or nitrogen was of the same order of magnitude. Since rubbers including NR are known to have high gas permeabilities, PTI seems to have good enough permeability for the application on human skin.

Conclusion

The synthetic conditions of AT-PTs and ionene polymers therefrom were established for those having various molecular weight of poly(oxytetramethylene). Together with excellent tensile properties and very good gas and moisture permeabilities of PTI film, its high adhesiveness to a Bakelite surface suggests us that PTI can be a candidate of adhesives for biomedical applications. This view is further supported by the following researches: It is very well known that PTMG based poly(urethane)s are blood compatible,[6–8] and ionene-type polymers have been considered for biomedical applications.[18–20] The possibility on this line will be investigated and be reported later.

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