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DIELECTRIC RELAXATION IN A SERIES OF HETEROPHASE POLYETHER POLYURETHANES

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Abstract—The dielectric spectra of a number of polyether polyurethanes, measured in the region of the lower glass transition temperature, have been discussed in terms of a two-phase structure. The highest frequency process has been ascribed to segmental rotation of the polyether blocks in the soft phases. The activation energies for this process were obtained and found to be close to those for the polyether homopolymers.

Variations in the distribution of relaxation times and in the glass transition temperatures with polymer composition suggest that the urethane segments exert considerable influence on the mobility of neighbouring polyether groups.

INTRODUCTION

THE STRUCTURE of thermoplastic polyurethane elastomers has been the subject of intensive investigation(1) by a number of techniques. The picture which has emerged(2) is that of a two-phase domain structure in which hard urethane-rich regions act as physical cross-links for a rubber matrix. These elastomers differ from the styrene–butadiene block copolymers, to which a similar domain structure has been ascribed, in that the block lengths involved in the polyurethane case are much shorter. Presumably this is due to the much stronger intermolecular interactions in the polar copolymers.

Hydrogen bonding is important in polyurethane elastomers;(3) it appears that urethane–urethane bonding is favoured although urethane–ether links are also possible. This latter type of hydrogen bond provides a mechanism whereby segmental mobility of ether or ester chain segments may be modified by proximity to urethane segments. Such interactions might arise by inefficient phase separation or at domain boundaries.(4) The aim of this study was to extend earlier observations(5,6) of dielectric relaxation in polyurethane elastomers to two series of polyether polyurethanes so as to ascertain the way in which mobility in the flexible polyether block depends upon chain composition.

Early studies(5) of dielectric relaxation in these polymers showed that any orientation polarization was swamped by a Maxwell–Wagner–Sillars(7–9) interfacial polarization. This type of polarization has been found in a number of systems and has been reviewed recently.(10,11) However, stringent purification of the polyether polyurethanes reduces the concentration of charge carriers to the point where four dielectric processes may be observed.(6) These are (in order of increasing frequency of observation) polarization at sample–electrode interfaces, polarization at domain boundaries, a.c. conduction and orientation polarization of polyether segments. In this paper, emphasis is placed on the domain interfacial polarization and the polyether orientation polarization.

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EXPERIMENTAL

Polymers were prepared by the reaction of methylene bis(phenyl isocyanate) with polyethylene oxide or polypropylene oxide diols and were chain-extended with butane 1,4-diol. The technique has been described by Lyman.(1,2) Polymers were reprecipitated three times from dimethyl formamide into water and then three times from chloroform into methanol. The polymers were then dried to constant weight under vacuum at 60° and compression moulded(5) at 80°. Metal electrodes were placed on the samples either by evaporation under vacuum (gold or aluminium) or by including aluminium foil in the compression moulding.

For convenience, the samples are named with the initial letter (E, ethylene; P, propylene) and the number average molecular weight of the polyether diol. The polymers, together with comments on the method of chain extension, the glass transition temperatures of the polyether phases and weight average molecular weights are listed in Table 1.

The molecular weights were obtained using a Sofica light-scattering photo-diffuso-goniometer; glass transition temperatures were measured using a Perkin–Elmer DSC-1B differential scanning calorimeter. Dielectric measurements over the frequency range 10^{-5}–10^{6} Hz were made as described previously.(5,6) The transformation of d.c. transient measurements to equivalent low frequency parameters was carried out as described previously.(6)

TABLE 1

Polymer	Comments	T_g (soft phase), (K)	$\bar{M}_w \times 10^{-5}$
E 206 (a)	Not extended with butanediol	306	1·04
E 206 (b)	Butanediol added to polyether–diisocyanate oligomer	321	39
E 400	Butanediol added to polyether–diisocyanate oligomer	282	78
E 340	Polyether added to butanediol–diisocyanate oligomer	259	4·6
P 400	Butanediol added to polyether–diisocyanate oligomer	318	104
P 1000	Butanediol added to polyether–diisocyanate oligomer	257	0·72
P 1025	Diols mixed and added to diisocyanate	255	11·1
P 1670 (a)	Polyether added to butanediol–diisocyanate oligomer	220	7·1
P 1670 (b)	Butanediol added to polyether–diisocyanate oligomer	223	9·7
B	Butanediol reacted with diisocyanate	382(13)	20
E	Polyethylene oxide	206(14)	—
P	Polypropylene oxide	198(14)	—

RESULTS

Four processes have been observed in all polymers over the frequency range examined.

1. *The lowest frequency process*

A loss process is observed at the lowest frequencies (10^{-5}–10^{-1} Hz) and highest temperatures. This loss is very dependent on temperature, electrode material, water absorption by the sample and charging voltage. Despite experimental difficulties associated with the measurement of small currents at long times (estimated as 40 per cent in ϵ'' at 10^{-5} Hz), there is every reason to believe that this is a real phenomenon and not a manifestation of base-line drift in the recording equipment. The same behaviour has been observed(11,15) in other polymers.

The loss phenomenon is largest when the electrode–sample contact is most efficient, and is least pronounced when electrodes are pressed on to the surface in the moulding process. Since the loss varies approximately as T/V where V is the charging voltage, the process is ascribed to the build-up and decay of charge at blocking electrodes as predicted for the case of thin films by Stern and Weaver.(16) Examples of this phenomenon are given in reference (6), but it is given no further consideration in this work.

2. *Maxwell–Wagner–Sillars Polarization*(6)

An example of the dielectric loss, ϵ'', and increment in the real permittivity, $\Delta\epsilon'$, due to this process is illustrated in Fig. 1. The phenomenon is very dependent on the impurity level and thermal prehistory of the sample, but is independent of charging voltage and electrode material. The magnitude of the loss is proportional to the d.c. bulk conductivity (Fig. 2) and exhibits the same temperature-dependence.

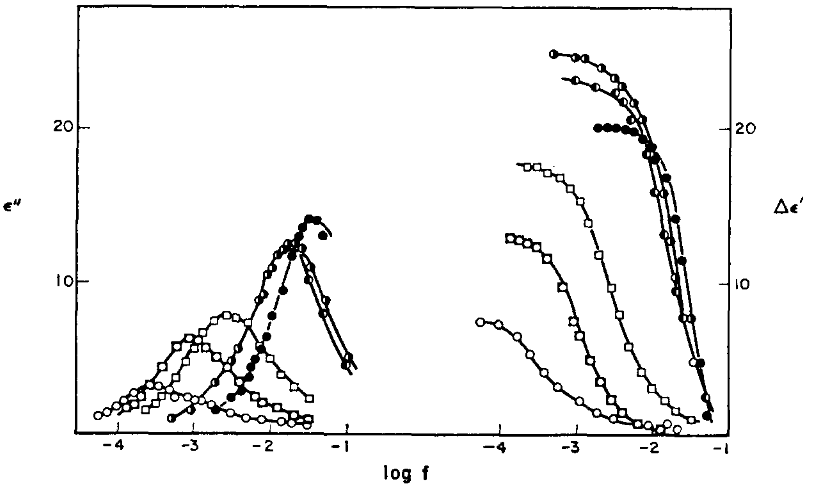

FIG. 1. Maxwell–Wagner–Sillars polarization in poly(propylene oxide)-polyurethane. P 400. ● 63°, ◑ 58° (measured by charging transient), ◐ 58° (measured by discharging transient), □ 49°, ■ 45°, ○ 40°.

The loss peak due to this process was clearly resolved from the lower frequency phenomenon in the polymers E 206 (b), E 400, P 400, P 1000 and P 1025. In these cases, measurements were made at a variety of temperatures close to the glass temperature of the continuous phase; values of the relaxation frequency and loss magnitude at a convenient temperature are quoted in Table 2. In all cases, the increment in ϵ' due to the polarization was approximately $2\epsilon''_{max}$ as would be expected for a process obeying the ideal Debye equations (which is the case for idealised Maxwell–Wagner polarization).

While a consistent relationship between dielectric loss and bulk conductivity was found for each sample at different temperatures (as Fig. 2), no single relationship between these parameters covered all the samples. Both conductance and loss are

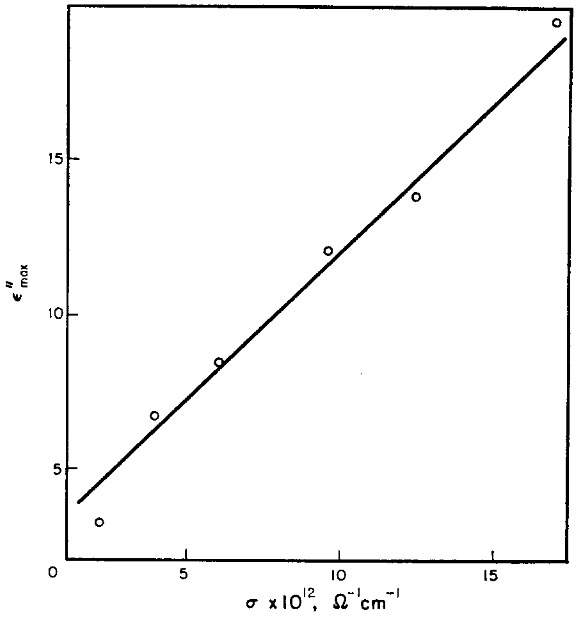

FIG. 2. Maxwell-Wagner-Sillars loss compared with bulk conductivity for poly(propylene oxide)-polyurethane P 400 at various temperatures.

TABLE 2. MAXWELL-WAGNER-SILLARS INTERFACIAL POLARIZATION LOSSES

Polymer	Temp. (°C)	ϵ''_{max}	$f_{max} \times 10^4$ (Hz)	$\sigma \times 10^{12}$ (bulk d.c. conductivity) ($ohm^{-1}\ cm^{-1}$)
E 206 (a)	30	7·0	20	1·0
E 400	20	2·0	100	—
P 400	40	3·3	3·0	1·0
P 1000	12·5	2·2	150	22
P 1025	30	6·0	14	4·4

negligible ($\sigma \sim 10^{-1}$ ohm^{-1} cm^{-1}, $\epsilon'' \sim 10^{-1}$) below the glass temperature of the mobile phase.

3. *Dipole orientation polarization*

a.c. Bridge measurements on these polymers show two phenomena,(6) a conductance loss at the lowest frequencies (10^0–10^3 Hz) and a dipole orientation process. The latter process can be observed also at low frequencies (in the d.c. transient region) when the temperature is reduced towards the glass temperature of the mobile phase. Measurements in the frequency plane on poly(propylene oxide)-polyurethane P 1025 (Fig. 3) illustrate this point. The complex plane diagram of ϵ' against ϵ'' for this polymer (Fig. 4) illustrates the asymmetric curves typical of all these polyurethanes.

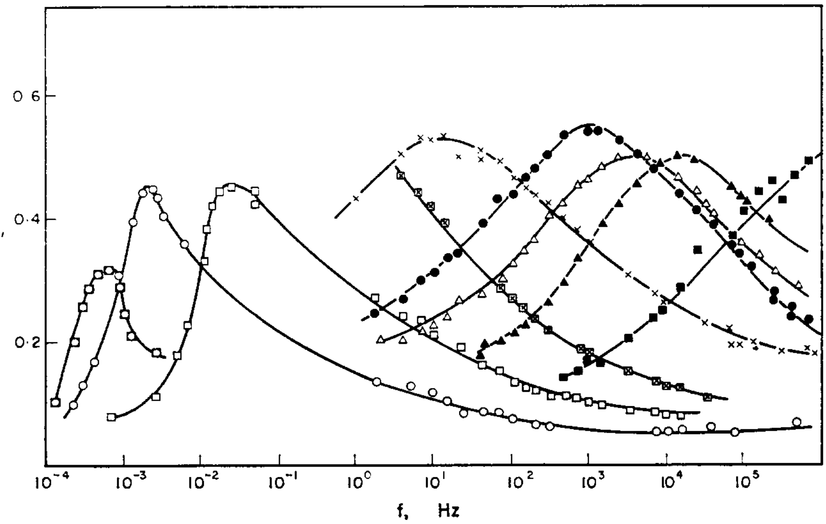

FIG. 3. Dipole orientation polarization loss in poly(propylene oxide)–polyurethane. P 1025. ▣ −27°, ○ −20·5°, □ −15°, ⊠ −6·5°, × 0°. ● +19·5°, △ +25°, ▲ +36°, ■ +63°.

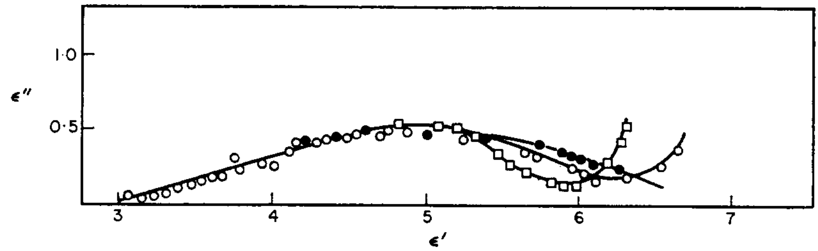

FIG. 4. Complex plane diagram of dipole orientation process in poly(propylene oxide)–polyurethane. P 1025. ● −15°, ○ +36°, □ +63°.

The relaxation frequencies for the poly(ethylene oxide) and poly(propylene oxide) polyurethanes are presented in the form of Arrhenius diagrams (Figs. 5 and 6, respectively). The plots are non-linear, but the slope at 10^0 Hz was used to calculate an apparent "activation energy" and these, along with the Cole–Davidson distribution parameters, are listed in Table 3.

TABLE 3. DIPOLE ORIENTATION RELAXATION PARAMETERS

Polymer sample	ΔH (kJ mol^{-1})	Relaxation distribution parameter
E 206 (a) without electrodes	210	0·28
E 206 (a) with evaporated gold electrodes	230	0·28
E 206 (b)	190	0·28
E 400	197	0·22
P 400	193	0·34
P 1000	155	0·24
P 1025	155	0·21
P 1670 (a)	125	0·20
P 1670 (b)	125	0·20

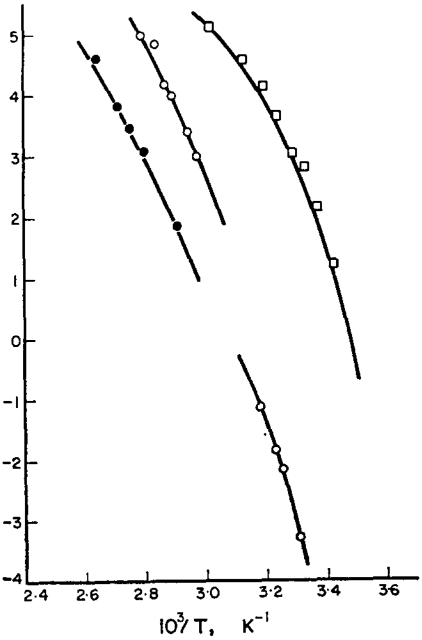

Fig. 5. Dipole orientation frequencies of poly(ethylene oxide)–polyurethanes. (i) Gold electrodes after annealing; (ii) without electrodes before annealing. ○ E 206 (a) ● E 206 (b) □ E 400.

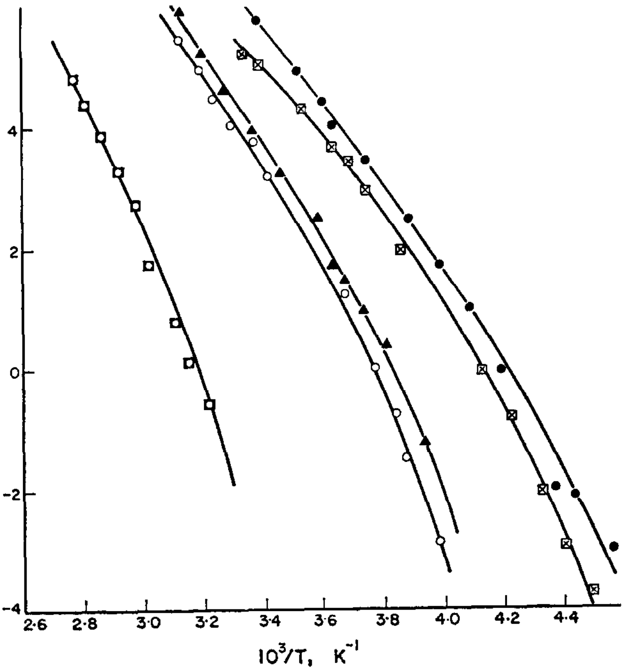

Fig. 6. Dipole orientation frequencies of poly(propylene oxide)–polyurethanes. □ P 400, ○ P 1025, △ P 1000, ☒ P 1670 (a) ● P 1670 (b).

DISCUSSION

1. *The Maxwell–Wagner–Sillars process*

The origin of the process ascribed to Maxwell–Wagner–Sillars interfacial polarization seems well founded on the basis of the known two-phase structure of such polymers, the dependence on conductance characteristics and thermal prehistory of the sample, and independence of sample–electrode interface parameters. The characteristics of this phenomenon are known to depend upon the volume fraction and shape of the occluded phase and the permittivity and conductivity of the two phases.

In deciding which constitutes the more highly conducting phase, it is noteworthy that the loss process is negligible below the glass transition temperature of the continuous rubber phase, that its magnitude is proportional to the d.c. bulk conductivity which must involve the continuous phase, and that the conductivity of the polyether phase above its glass temperature is greater than that of the urethane-rich phase below its glass temperature (as observed on pure polyether and butane-diol diisocyanate polymers). Thus the charge carriers must migrate either in the continuous polyether phase or in a diffuse region corresponding to the inter-phase boundaries. Unfortunately, the permittivities, loss magnitudes, and frequencies observed here do not fit the equations of Sillars(9) for dilute suspensions of non-spherical occlusions or those of Hanai(17) for more concentrated suspensions of spherical occlusions. Consequently, the shape and perfection of the occlusions cannot be deduced from these loss measurements. However, the sensitivity to thermal prehistory and annealing, combined with the magnitude of the phenomenon, do suggest that the occlusions are non-spherical and that the phase-boundaries may be diffuse rather than infinitely sharp.

2. *The polyether dipole orientation process*

The conclusion that this process is associated with segmental rotation of the polyether chain sections is supported by (i) the correspondence between the relaxation temperatures at 10^0 Hz and the glass transition temperatures of the rubbery phase as measured by differential scanning calorimetry: (ii) the change in magnitude of the loss process between polymers E 206 (a) and E 206 (b) where approximately half the polyether sections are replaced by non-polar butane-diol moieties: (iii) the regular variation in the temperature–frequency location of the process with changes with polyether type and section length: (iv) the curvature of the Arrhenius plots which is characteristic of a backbone segmental orientation process.

The "activation energies" for dipole orientation polarization in pure poly(ethylene oxide)(18) and poly propylene (oxide)(19) can be estimated from published data as 210 and 130 kJ mol^{-1}, respectively. Thus it can be seen that the presence of urethane groups exerts a more restricting influence on the short chain poly(propylene oxide) sections than on the poly(ethylene oxide), and that in the former case the freedom of movement enjoyed in pure polyether is not attained until longer segment lengths.

The relaxation magnitudes have been analysed using the method of Frohlich(20)

$$\frac{(\epsilon'_0 - \epsilon'_\infty)(2\,\epsilon'_0 + \epsilon'_\infty)}{\epsilon'_0(\epsilon'_\infty + 2)^2} = \frac{4\,\pi N}{9\,kTV}\,g\mu^2$$

to yield the quantity $g\mu^2$ per repeat unit of the polymer chain. Here μ is the unit dipole moment and g is the Kirkwood correlation parameter.

The values of ϵ'_0 and ϵ'_∞ were taken from the intercepts of the Cole–Cole diagrams and N/V, the number of repeat units per unit volume, were calculated from the chain compositions and densities. These values have been compared with the corresponding values calculated for the polyether chains using the data of Loveluck.(21) In this case, when n is the number of ether units in the polyether section, the quantity $g_E n \mu_E{}^2$ can be calculated using $1 \cdot 15\ D^2$ for $\mu_E{}^2/n$ for poly(ethylene oxide) and $1 \cdot 05\ D^2$ for $\mu_E{}^2/n$ for poly(propylene oxide). The comparison of the observed $g\mu^2$ per repeat unit and $g_E n\mu_E{}^2$ calculated for the polyether chain in each repeat unit is illustrated in Fig. 7. With the exception of polymers P 400 and P 1670 (a), there is a 1–1 correspondence, confirming that in general the relaxing dipoles reside in the polyether chain sections, and that the very polar urethane groups are effectively immobile.

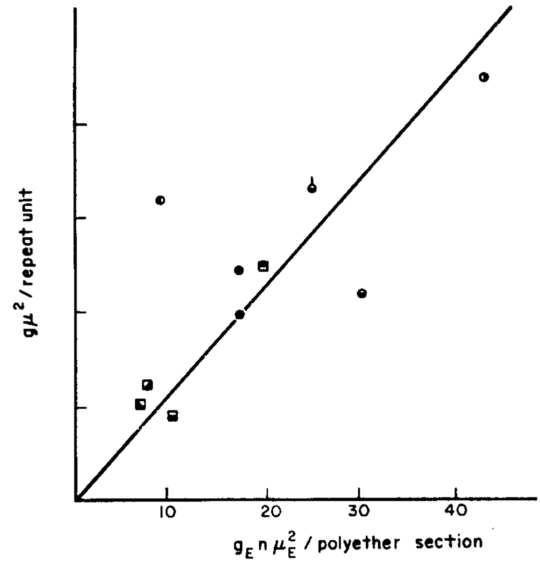

FIG. 7. Observed dipole moment per repeat unit compared with the calculated dipole moment per polyether section in each repeat unit. ◪ E 206 (a), ◩ E 206 (b), ⬓ E 400, ⬒ E 340, ◐ P 400, ◒ P 1000, ● P 1025, ◒ P 1670 (a), ◑ P 1670 (b).

In discussing the movement of the polyether sections, it is necessary to take account of the fact that the relaxation magnitudes calculated from ϵ'_0 suggest that each ether oxygen is free to move, but reduced frequencies of movement and higher activation energies are observed in the shorter polyether chains. The conclusion must be that movement of ether groups neighbouring the urethane domains is retarded, but not totally removed, above the glass transition temperature of the rubber phase. On this basis, the increase in the breadth of distribution of relaxation times with increasing polyether chain length can be rationalised in terms of ether units remote from urethane groups (present only in the longer chains) being characterised by shorter relaxation times than groups within two or three units of the urethane domains.

The glass transition temperatures of the polymers closely follow the copolymer relationship in which the reciprocal transition temperature varies linearly with the weight per cent polyether, Fig. 8. Again, this is in accord with a much retarded movement of ether segments in proximity to urethane sections.

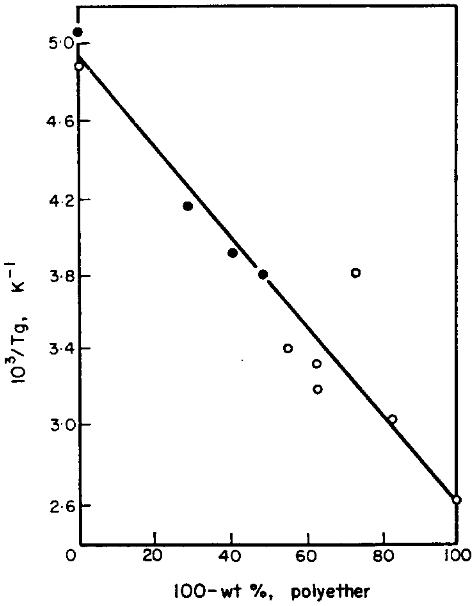

FIG. 8. Reciprocal glass transition temperature of polyether polyurethanes. ○ poly(ethylene oxide) copolymers. ● poly(propylene oxide) copolymers.

REFERENCES

(1) G. M. Estes, S. L. Cooper and A. V. Tobolsky, *J. Macromol. Sci.* **C4,** 313 (1970).
(2) J. A. Koutsky, N. V. Hien and S. L. Cooper, *J. Polym. Sci.* **B8,** 353 (1970).
(3) R. W. Seymour, G. M. Estes and S. L. Cooper, *Polymer Preprints* **11,** 867 (1970).
(4) R. Bonart, *J. Macromol. Sci.* **B2,** 119 (1968).
(5) A. M. North, J. C. Reid and J. B. Shortall, *Europ. Polym. J.* **5,** 565 (1969).
(6) S. B. Dev, A. M. North and J. C. Reid, *Polymer Preprints* **12,** 142 (1971); in *Dielectric Properties of Polymers*. Plenum Press, New York (1972).
(7) J. C. Maxwell, *Electricity and Magnetism* Vol. 1, p. 452. Clarendon Press, Oxford (1892).
(8) K. W. Wagner, *Arch. Electrotech.* **2,** 378 (1914).
(9) R W. Sillars, *J. Inst. Elect. Engineers*, **80,** 378 (1937).
(10) L. K. H. van Beck, *Progress in Dielectrics*, edited by J. B. Birks and J. Hart, Vol. 7. Heywood, London (1967).
(11) M. E. Baird, G. T. Goldsworthy and C. J. Creasey, *Polymer* **12,** 159 (1971).
(12) D. J. Lyman, *J. Polym. Sci.* **45,** 49 (1960).
(13) W. J. MacKnight, M. Young and T. Kajiyama, *Polymer Preprints* **9,** 860 (1968).
(14) *Polymer Handbook*, edited by J. Brandrup and E. H. Immergut. Wiley, New York (1966).
(15) S. Hirota, S. Saito and T. Nakajima, *Kolloid Z.* **213,** 109 (1966).
(15) S. Hirota, S. Saito and T. Nakajima, *Kolloid Z.* **213,** 109 (1966).
(16) F. Stern and C. Weaver, *J. phys. Chem.* **3,** 1736 (1970).
(17) T. Hanoi, *Bull Inst. Chem. Res., Kyoto Univ.* **39,** 341 (1961).
(18) Y. Ishida, M. Matzuo, S. Togami, K. Yamafugi and M. Takayanagi, *Kolloid Z.* **183,** 74 (1962).
(19) G. Williams, *Trans. Faraday Soc.* **61,** 1564 (1965).
(20) H. Frohlich, *Theory of Dielectrics*. Oxford University Press, London (1949).
(21) G. D. Loveluck, *J. chem. Soc.* 4729 (1961).

Résumé—On discute, en termes de structures à deux phases, les spectres diélectriques de plusieurs polyéther polyuréthanes, mesurés dans la région de la température de transition vitreuse la plus basse. Le processus de fréquence la plus élevée a été attribué à la rotation des segments de polyéther dans la phase non vitreuse. On a obtenu les énergies d'activation de ce processus et on a trouvé que leur valeur était voisine de celle des polyéthers homopolymères.

Les variations dans la distribution des temps de relaxation et des températures de transitions vitreuses suggèrent que les segments uréthane exercent une influence considérable sur la mobilité des groupements polyéther voisins.

Sommario—Si sono discussi in termini di una struttura bifase, gli spettri dielettrici di un certo numero di poliuretani di polietere, misurati nel campo della temperatura inferiore di transizione vetrosa. Si è attribuito il processo ad alta frequenza alla rotazione settoriale dei blocchi di polietere nelle fasi soffici. Si è trovato che le energie di attivazione per tale processo sono vicine a quelle per gli omopolimeri di polietere.

Le variazioni nella distribuzione dei tempi di rilassamento e nelle temperature di transizione vetrosa che si hanno con la composizione del polimero, fanno supporre che i segmenti di uretano esercitano un'influenza considerevole sulla mobilità dei gruppi di polieteri vicini.

Zusammenfassung—Die dielektrischen Spektren einer Anzahl von PolyätherUrethanen, die im Bereich der unteren Glasumwandlungstemperatur gemessen wurden, wurden bezüglich einer Zweiphasenstruktur diskutiert. Der Prozess bei der höchsten Frequenz wurde der Rotation der Segmente der Polyätherblocke in den weichen Phasen zugeordnet. Die Aktiverungsenergien für diesen Prozess wurden erhalten und liegen nahe bei denen von Polyäther Homopolymeren.

Unterschiede in der Verteilung der Relaxationszeiten und in den Glasumwandlungstemperaturen mit der Zusammensetzung der Polymeren lassen darauf schließen, daß die Urethansegmente einen beträchtlichen Einfluß auf die Beweglichkeit der benachbarten Polyäthergruppen ausüben.