Table I
τ_1^0/τ_k for Polystyrene Solutions

M	c, g cm^{-3}	solvent[a]	method[b]	τ_1^0/τ_k	ref
2.33×10^5	0.40	CB	CP	1.55	c
	0.50	CB	TT	2.0	c
6.70×10^5	0.30	CB	CP	3.5	c
	0.40	CB	TT	6.7	c
9.50×10^5	0.20	CB	CP	3.0	c
	0.30	CB	TT, CP	7.5	c
	0.40	CB	TT	11	c
1.80×10^6	0.276	CB	CP	24	d
5.60×10^6	0.221	DEP	CP	54	d
7.60×10^6	0.176	DEP	CP	65	d
	0.221	DEP	CP	86	d

[a] CB stands for chlorinated biphenyl and DEP for diethyl phthalate. [b] CP stands for the method using a cone-and-plate type relaxometer and TT the method utilizing the tensile tester as explained in text. [c] Present study. [d] Reference 4.

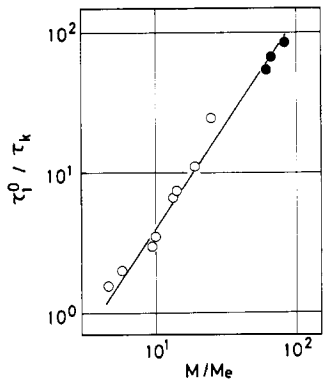

Figure 1. τ_1^0/τ_k plotted against M/M_e, the number of entanglements per molecule for polystyrene solutions. Filled circles are for solutions in diethyl phthalate and unfilled circles in chlorinated biphenyl. Slope of line is 1.5.

the graph where the shear stress was plotted against time with log–log scales.[1] The values of τ_1^0 and τ_k are not separately shown in Table I. These values were much affected by the slight error in concentration that was caused by the long waiting time to eliminate bubbles from the sample. The variation of the ratio τ_1^0/τ_k with the slight change of concentration was negligible: The same value was obtained for different batches of the solution. Table I also includes the results reported previously.[1]

The ratio τ_1^0/τ_k is plotted against M/M_e with log–log scales in Figure 1. Here M_e was determined with eq 2. The unfilled circles represent the solutions in chlorinated biphenyl and the filled circles in diethyl phthalate. The line is drawn with a slope 1.5. Obviously most of the data points lie close to the solid line. We may conclude that the tentative equation (1) should be replaced with (3). The previous conclusion was based on the four points at the top of the figure and was affected too much by the fourth point from the top. The present result implies that the quantity τ_k is proportional to $(M/M_e)^2$ and hence it may be closely related to the quantity T_{eq} derived from the tube model theory.

One may dispute the appropriateness of eq 2. Several theories support the relation that[3,8]

$$M_e \propto c^{-a} \qquad a > 1 \tag{4}$$

at relatively low concentrations. However, one may presume that $M_e \propto c^{-1}$ at high concentrations.[8] Thus it may be plausible to use eq 2, which approximately represents many experimental data,[9] for the present solutions with relatively high concentrations. Experiments at lower concentrations will be necessary to investigate the appropriateness of eq 4.

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SAXS Studies of Segmented Polyether Poly(urethaneurea) Elastomers

Considerable efforts have been directed at understanding the structure–property relationships in many block and segmented copolymer systems. Much of this work has been undertaken on the segmented polyurethane and segmented poly(urethaneurea) systems as a result of their high commercial utilization. Of interest are the nature of the domain structure and the variation in morphological texture of these systems in bulk form that possess different composition or fabrication history.

In a series of recent papers the properties of segmented poly(urethaneureas) based on 2,4-TDI with poly(tetramethylene oxide), PTMO, as the soft segment and ethylenediamine as chain extender have been extensively studied by Sung and co-workers.[1-3] In general, considerable improvement in the extent of phase segregation was suggested by a much lower T_g of the soft-segment phase and a much higher T_g of the hard-segment domains in poly(urethaneureas) extended with ethylenediamine rather than with butanediol. IR spectra of two polyether poly(urethaneureas) with 1000 and 2000 molecular weight PTMO suggest the presence of three-dimensional hydrogen bonding within their hard-segment domains, where one urea carbonyl is bonded to two NH groups. The interface between the domain and the soft matrix was suggested to be quite sharp since most of the urethane carbonyl is free from bonding; i.e., unbonded carbonyl existed. In addition, mechanical properties implied that, at the same urea content (30% by weight of hard segment), the domains in the PTMO-1000 sample are more interconnected than those in the PTMO-2000 sample and that the soft-segment phase of the former may contain more solubilized hard segment than that of the latter.[2] That is, the PTMO-2000 sample was believed to exhibit better phase separation and consequently to account for better mechanical properties such as higher elongation to break, greater toughness, lower hysteresis, and a slower rate of stress relaxation, even though ultimate tensile strength is slightly lower. The current work investigates the morphology of these same urea-based urethanes by small-angle X-ray scattering and,

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Table I
Properties and SAXS Analysis of Polyether Poly(urethaneurea) Samples

sample	polymer M_n	soft-segment M_w	hard-segment content,[a] wt/(ED + TDI)	soft-segment T_g[b]	hard-segment T_g[b]	$10^{-3}\langle\rho^2\rangle$[c]	interfacial thickness E[d]	Bragg spacing d[d]	d[d] (1-D correlation function)
PTMO-30-1000	21 000	1000	30	−53	192	5.58	5	122	107
PTMO-30-2000	34 000	2000	30	−74	190	7.14	3	140	121
PTMO-54-1000	43 000	1000	54	−55	180	17.5	9	130	115

[a] In percent. [b] °C. [c] (mol electron)/cm³. [d] Å.

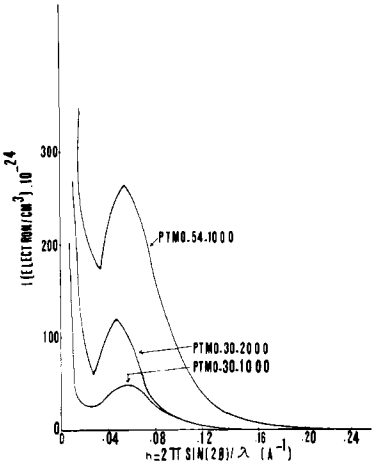

Figure 1. SAXS scans of polyether poly(urethaneurea) samples.

in general, further supports some of the earlier data obtained from the mechanical and thermal tests by Sung et al.

A standard Kratky small-angle X-ray camera was utilized for the SAXS experiments. The X-ray source was a Siemens AG Cu40/2 tube operated at 40 kV and 25 mA by a GE XRD6 generator. The counting of X-ray intensity was performed by a Siemens sealed proportional gas detector in conjunction with a pulse height analyzer. The camera motor was controlled by a PDP 8/a computer, which also served for initial data reduction. The SAXS data were analyzed by Vonk's computer program.[4] Further details of the experimental technique and analysis have been given elsewhere.[5,6]

The synthesis of polyether poly(urethaneureas) was described in earlier papers by Sung and co-workers.[1-3] Thin films were cast from dimethylformamide solution onto glass, followed by drying in a vacuum oven at 50 °C for at least 2 days to remove any traces of solvent. The material was allowed to age at room temperature for at least 2 weeks before any experiments were carried out. Table I summarizes the properties and the composition of the samples tested.

Samples PTMO-30-1000, PTMO-30-2000, and PTMO-54-1000 were studied by SAXS to determine the effect of the urea linkage and of increasing the molecular weight of the soft segment on final bulk morphology. The desmeared SAXS scans of the three samples are presented in Figure 1. The three curves differ both in the scattered intensity and in the position of the side peak. Application of Bragg's law yields periodicities of 122 (12.2n), 140 (14.0n), and 130 Å (13.0n) for PTMO-30-1000, PTMO-30-2000, and PTMO-54-1000, respectively (Table I). The structure of the material is not totally random because, in all the samples, the three-dimensional correlation function, $\gamma(r)$, was not completely exponential in behavior (Figure 2). Another important observation was that the one-dimensional function, $\gamma(x)$, displays periodicity (Figure 3), indicating that the two-phase structure can be described as alternating layers of soft and hard segments whose spacing is given by the calculated periodicity.[1,5] The periodicities obtained from the location of the first peak in the one-dimensional correlation function are 107, 121, and

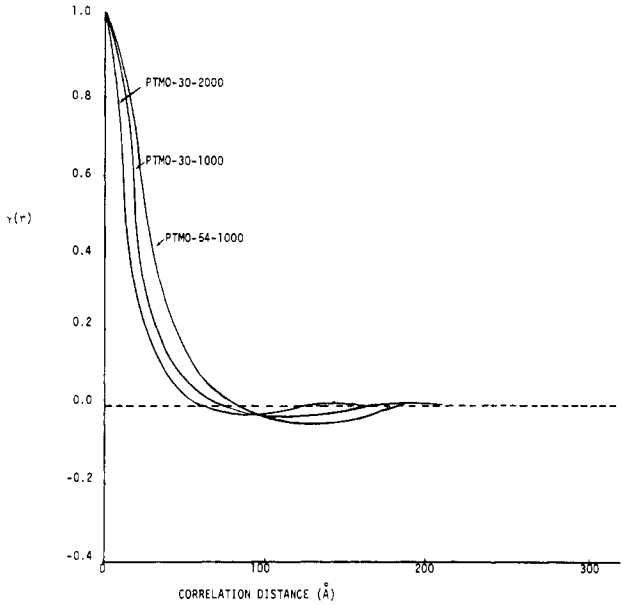

Figure 2. Three-dimensional correlation function of poly(urethaneurea) samples.

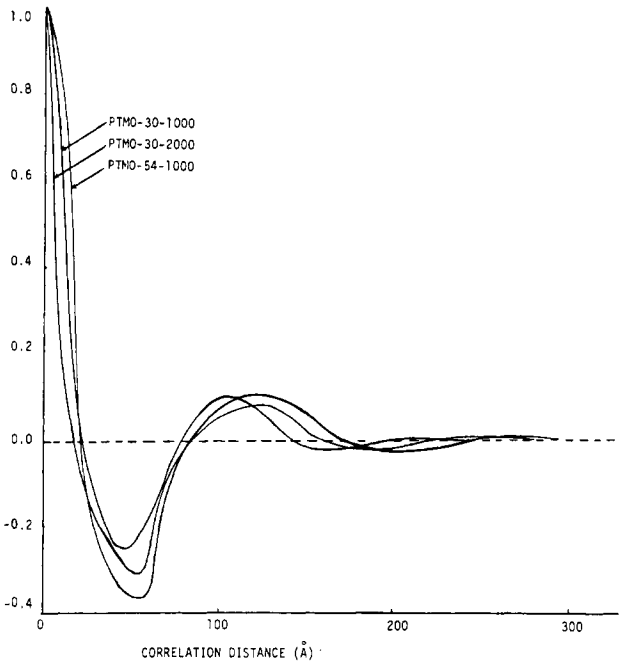

Figure 3. One-dimensional correlation function of poly(urethaneurea) samples.

115 Å for PTMO-30-1000, PTMO-30-2000, and PTMO-54-1000, respectively (Table I). The mean-square fluctuation in electron density $\langle \rho^2 \rangle$, is also listed in Table I for the three samples. For different urea content and constant soft-segment molecular weight (PTMO-30-1000 and PTMO-54-1000), $\langle \rho^2 \rangle$ increases with increasing urea fraction as expected. However, for the same composition but with different soft-segment molecular weight, PTMO-30-2000 shows a higher $\langle \rho^2 \rangle$ value than PTMO-30-1000, strongly implying better phase separation. This directly supports the earlier conclusion of Sung et al. based on their mechanical and thermal studies. The improvement in the domain texture of PTMO-30-2000 over that of PTMO-30-1000 could be attributed to increasing the thermodynamic incompatibility of the hard and the soft blocks due to the higher soft-segment molecular weight. That is, the Flory–Huggins χ parameter is molecular weight dependent and increases as the soft-segment molecular weight increases.[7]

A second area of interest is that of the effect of altering the morphology and the material by using ethylenediamine as the chain extender rather than butanediol. We have attempted to shed some light on this topic by determining the interfacial thickness of the domains using the SAXS method of Ruland.[8] Our analysis (see Table I) does indeed suggest that the diamine promotes somewhat better phase separation in that the boundary thickness values are somewhat less than those for the butanediol-containing systems. Specifically, earlier work of one of the authors[5] showed that the latter systems of equivalent hard-segment contents tend to provide interfacial thickness values on the order of 7–12 Å when the SAXS data are analyzed in an identical manner. However, one must be cautious to readily attribute major differences in properties between these two extenders to this interfacial or "mixing" argument alone. Specifically, there is also an inherent difference in molecular flexibility of the two extenders that may well contribute to property difference. This flexibility difference can be indirectly noted from the work of Bonart et al.,[9] who found that the hard-segment T_g based on MDI and diamine systems decreases from 187 °C when using ethylenediamine as an extender and to 179 °C for butylenediamine. In another study, Critchfield et al.[10] found that for a systematic series of linear aliphatic glycol extenders ranging in methylene content from 2 to 12, the modulus of the associated 2000 M_n poly(caprolactone)–MDI-based urethane passed through a minimum with seven methylene groups (1,7-heptanediol). Their explanation for this observed change in mechanical stiffness was based on changes in both phase separation and intermolecular interactions. Therefore, a significant point of argument may also be associated with the major change in flexibility, i.e., due to the increase in the first few methylene units. We suggest that the work of Sung et al. and their explanation may need to be modified by this consideration.

In summary, we believe that the SAXS results presented here lend more direct support to several of the earlier conclusions of Sung et al. regarding the effect of soft-segmented molecular weight on phase separation. However, some modification in thought may be useful to help explain the effect of the chain extenders on properties used in these same studies.

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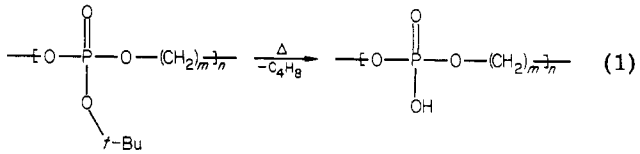
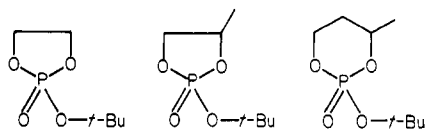
Novel Synthesis of Acidic Polyesters of Phosphoric Acid by Thermal Elimination of Isobutylene from Poly(alkylene *tert*-butyl phosphates)

The synthesis of high molecular weight poly(alkylene phosphates) is valuable for entry to functional polymers having a backbone analogous to the backbone of polynucleotides. There is also much interest in specific physical properties, e.g., hydrophilicity, inflammability, and thermal stability.[1] Synthetic routes reported so far are limited to (1) the synthesis of poly(ethylene phosphate) by removal of the quaternary ammonium salt with cation exchange resins from the polysalt of poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) and (2) the oxidation of poly(1,3,2-dioxaphosphorinane 2-oxide) with nitrogen dioxide.[2]

We report here a novel facile method for preparation of a series of poly(alkylene phosphates) by thermal elimination of isobutylene from poly(2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide), poly(2-*tert*-butoxy-1,3,2-dioxaphosphorinane 2-oxide), or their alkyl-substituted polymers which were synthesized by ring-opening polymerization of the cyclic phosphate (reaction 1). Although the preparative methods for five- and six-membered cyclic phosphates are well established,[3] the physical and chemical properties of *tert*-butoxy derivatives such as 2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide (**1**), 4-methyl-2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide (**2**), and 4-methyl-2-*tert*-butoxy-1,3,2-dioxaphosphorinane 2-oxide (**3**)





1 **2** **3**

are relatively unknown due to their thermal instability. These compounds are now successfully prepared by oxidation of the corresponding cyclic phosphite with N_2O_4 at

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