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$$dT_{g_i}/dP = dT_{g_j}/dP \qquad (R3)$$

for all *i*, *j*. From the entropic Ehrenfest relation[13] for the generic pure constituent and eq 34a, eq R3 gives eq 34b.
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Notes

Chain Propagation/Step Propagation Polymerization. 1. The Polymerization of Ethylene Oxide with an Acetal-Masked Initiator

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Structure control in copolymer synthesis is a continuing challenge for the polymer chemist, a situation that certainly holds true in the synthesis of segmented copolymers by conventional step polymerization techniques. Rarely does one attain a narrow molecular weight distribution for both segments within such copolymers, though this very goal is actively sought by at least two other research groups today.[1,2] In this research we are attempting the synthesis of highly regular segmented copolymers, i.e., those with narrow molecular weight distributions within each segment, by combining chain and step propagation procedures into one synthetic scheme. The thrust of this synthetic strategy focuses on synthesizing a highly regular telechelomer (a high molecular weight monomer) by anionic polymerization that in turn is converted into a copolymer of high molecular weight by step polymerization techniques. Figure 1 depicts the approach as it applies to segmented copolymers.

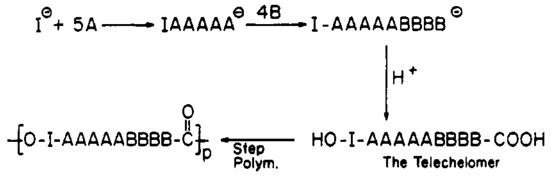

Figure 1. Illustration for chain/step polymerization using 5 "A" units and 4 "B" units.

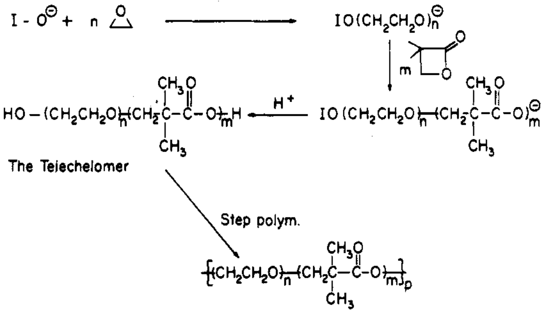

Figure 2. Chain/step synthesis of poly(oxyethylene-*co*-pivalolactone).

Let "A" represent the repeat unit within one segment and "B" the repeat unit within the other segment. The initiator, "I", contains a masked functionality that will be used later in step polymerization. Anionic (chain) initiation and polymerization leads to a monodisperse segment of monomer "A". Then either monomer "B" can be added directly or the nucleophilicity of the anion "A" can be altered prior to the addition of the second monomer to facilitate the formation of a monodisperse segment of "B". This new anion, the "B" anion, is then quenched by using chemistry that removes the mask from the initiator, thus creating the desired telechelomer, which can be rigorously purified at this point in the synthetic scheme, followed by mild condensation (step) polymerization to high polymer.

This methodology could be applied to a variety of "A" and "B" monomers to obtain a series of highly regular segmented copolymers containing segments of narrow molecular weight distributions. If the two segments are incompatible, the polymers will exhibit good phase separation and the surface of the polymer will be richer in the segment that has a lower surface energy. Proper selection of monomers, therefore, will lead to polymers having controlled surface properties such as biocompatibility, adhesion, and weathering. If one segment is hard and the other is soft, the segment lengths could be varied to obtain thermoplastic elastomers having good mechanical properties. The surface and mechanical properties of these copolymers could then be compared with those of ABA and AB block copolymers.

We have selected ethylene oxide (EO) and pivalolactone (PVL) as our first monomer pair. A general description of the chemistry used is shown in Figure 2. A masked initiator, I–O$^-$K$^+$, anionically polymerizes ethylene oxide, and the resulting anion is reacted with pivalolactone (PVL) to give a polymeric anion still containing the masked initiator fragment. The product is then acid hydrolyzed to give an oxyethylene–pivalolactone telechelomer, which on step polymerization will give the segmented copolymer.

In this paper we describe the chemistry needed to synthesize an acetal-masked potassium alkoxide initiator for the chain polymerization aspect of the research, and we describe how this acetal-masked initiator readily polymerizes ethylene oxide while keeping the mask in place. Acetal-masked lithioalkoxides have been previously reported by Schulz et al. for butadiene polymerization[3] and by Lefebvre for hexamethylcyclotrisiloxane polymerization.[4]

Experimental Section

Acetaldehyde 3-Chloropropyl Ethyl Acetal (1) and Its Organolithium Salt 2. The chloroacetal 1 was prepared according to the procedure of Eaton et al.,[5] using 3-chloro-1-propanol

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and ethyl vinyl ether. The product, 1, purified by vacuum distillation was a colorless liquid, bp 45 °C (5 mmHg). It was stored over powdered sodium carbonate at −30 °C. [^{1}H NMR ($CDCl_3$) 4.7 (1 H, q, CH), 3.8–3.2 (4 H, complex), 3.5 (2 H, t), 2.0 (2 H, pentuplet), 1.2 (3 H, d, CH_3), 1.1 ppm (3 H, t, CH_3). Conversion of 1 to 2 was done on a high vacuum line, using a modification of Eaton's procedure. A three-neck flask with a side-arm was connected to a round-bottom flask containing a break-seal. This apparatus was connected to the high vacuum line. The three-necked flask was equipped with a magnetic stirrer, a low-temperature thermometer, and a callibrated pressure-equalizing addition funnel. The addition funnel was topped with a short-path distillation apparatus, which was attached to another flask. The entire apparatus was flame-dried to 10^{-6} mmHg. Lithium (1 g, 0.13 mol) previously cleaned with hexane and 2-propanol were introduced under argon into the three-necked flask. At the same time, chloro acetal 1 (7.5 mL, 0.05 mol) was distilled into the addition funnel under vacuum. Dry ethyl ether (43 mL) was distilled into the three-necked flask through the main vacuum line. About 2 mL of 1 was added to the stirred mixture, and after 10–15 min, the lithium pieces became shiny in places, and the solution became cloudy. At this point, the three-necked flask was cooled and the temperature maintained between −5 and −15 °C. The remaining acetal was added dropwise over 1 h, and the mixture was stirred for another 7 h. In order to get rid of unreacted lithium pieces, the mixture containing 2 was poured into the attached round-bottom flask having the break-seal, and this flask was sealed off from the vacuum line.

Acetal Masked Alcohol 3. The round-bottom flask containing 2 was attached to the vacuum line through the break-seal, and ethylene oxide (2.5 mL, 0.05 mol) (previously dried over CaH_2 followed by drying over a potassium mirror) was distilled in. The mixture was stirred at 5 °C under argon for 30 min, and the resulting alkoxide was neutralized with degassed, deionizing water. The ether layer was separated and dried over sodium sulfate for 1 day. The acetal/alcohol 3 was recovered by fractional distillation (bp 70–80 °C (1 mmHg)).

Acetal Masked Initiator 4 and Polymerization of Ethylene Oxide. Conversion of 3 to 4 was also under vacuum (Figure 7). Potassium (6.0 g, 0.15 mole was twice distilled into a flask as a mirror, and 3 (5.4 mL, 0.03 mol) was distilled onto the mirror. The reaction was stirred at room temperature and degassed occasionally (hydrogen released) until the bubbling ceased (about 2 days) to give 4. THF (60 mL, dried over Na/K alloy) was distilled into the flask, and the contents were filtered through a coarse filter into ampules with break-seals.

The initiator 4 was introduced through a break-seal into a flame-dried round-bottom flask under high vacuum. Ethylene oxide (previously dried over CaH2) was twice distilled over potassium mirror into the flask, which was cooled to −78 °C. The mixture was stirred at room temperature for 4 days under dry argon (a mercury valve was used to avoid any sudden pressure release). Polymerization was terminated with degassed, deionized water. The acetal-capped polymer 5 was precipitated in cold ethyl ether and purified twice with dissolving in chloroform and precipitating in cold ether (Anal. Calcd; C, 55.19; H, 9.39. Found: C, 54.48; H, 9.29).

^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) were obtained with Varian XL-Series NMR superconducting spectrometer system and the 300-MHz ^{1}H spectrum was obtained, using Nicolet NT-300 spectrometer operating at a field of 7 T. All spectra were taken at room temperature in $CDCl_3$. A Waters GPC system containing a Model 6000A solvent delivery system, coupled with a R-401 differential refractometer, was used to obtain GPC chromatograms. Elemental analysis were done by Atlantic Microlab, Inc.

Results and Discussion

Synthesis of the Mixed Acetal/Alcohol 3. The synthesis was done on a vacuum line to prepare initiators and polymers of high purity, although it now appears that less stringent synthetic conditions could be employed. 3-(Chloropropyl)acetalaldehyde ethyl acetal (1) was prepared according to Eaton using 3-chloropropanol and ethyl vinyl ether[5] (Figure 3), and this acetal was converted to its lithium salt, 2, by directly reacting it with lithium, thus releasing lithium chloride. The lithium salts have a partially covalent character and they exist as aggregates in most common solvents.[6] In THF, the lithium salt does not polymerize ethylene oxide but adds only in a equimolar quantity to ethylene oxide, forming a lithium alkoxide.[7] In view of aggregations, this alkoxide is not suitable to prepare poly(oxyethylene) with a narrow molecular weight distribution, and as such, it was converted to a potassium alkoxide in the following steps. First, the lithium alkoxide was converted to the acetal/alcohol 3 by treatment with deionized, degassed water. This acetal/alcohol is a unique form of a diol, wherein one alcohol group is masked as an acetal and the other is not.

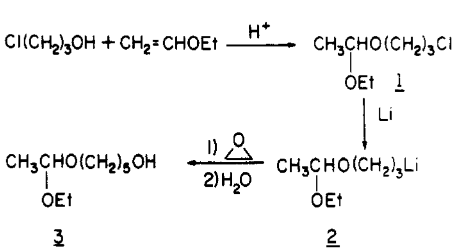


Figure 3. Synthesis of the masked acetal/alcohol 3.

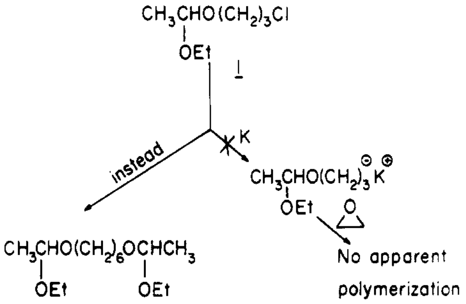


Figure 4. Ineffectiveness of the direct conversion of 1 to the potassium salt.

The potassium alkoxide, unlike the partially covalent lithium alkoxide, is ionic in character and as such it should polymerize ethylene oxide to give a polymer with a narrow molecular weight distribution. Initially we attempted to convert the chloroacetal 1 directly into the potassium salt by treating with potassium metal, but the product did not polymerize ethylene oxide. Even though some potassium alkoxide might have formed, previous evidence suggests that the major product was an alkane, formed by Wurtz coupling (Figure 4).[8,9]

^{1}H NMR (200 MHz) of the alcohol is shown in Figure 5. The triplet at 1.2 ppm and the doublet at 1.3 ppm represent the methyls coming from the acetal moiety of the alcohol, and the quartet at 4.8 ppm represents the methine proton from the acetal moiety. The two multiplets around 1.5–1.7 ppm represent "c" and "d" protons and the multiplet centered around 3.5 ppm represent "e" protons. The broad signal "f" is due to the alcohol proton; this signal disappears on addition of D_2O.

The 50-MHz ^{13}C NMR of the acetal alcohol (figure 6) confirms the peaks assignments in ^{1}H NMR. This is an attached-proton test (APT) spectrum which shows secondary carbons as downward signals and the tertiary and primary carbons as upward signals. The spectrum is referenced to solvent ($CDCl_3$) carbon at 77.0 ppm. The two methyl carbons "a" and "b" and the methine carbon "g" appear at 14.8, 20.0, and 99.5 ppm, respectively, as upward signals. The methylene carbons "e" attached to ether oxygens appear at 62.5 ppm and the methylene group attached to alcohol group appears at 60.5 ppm as downward signals.

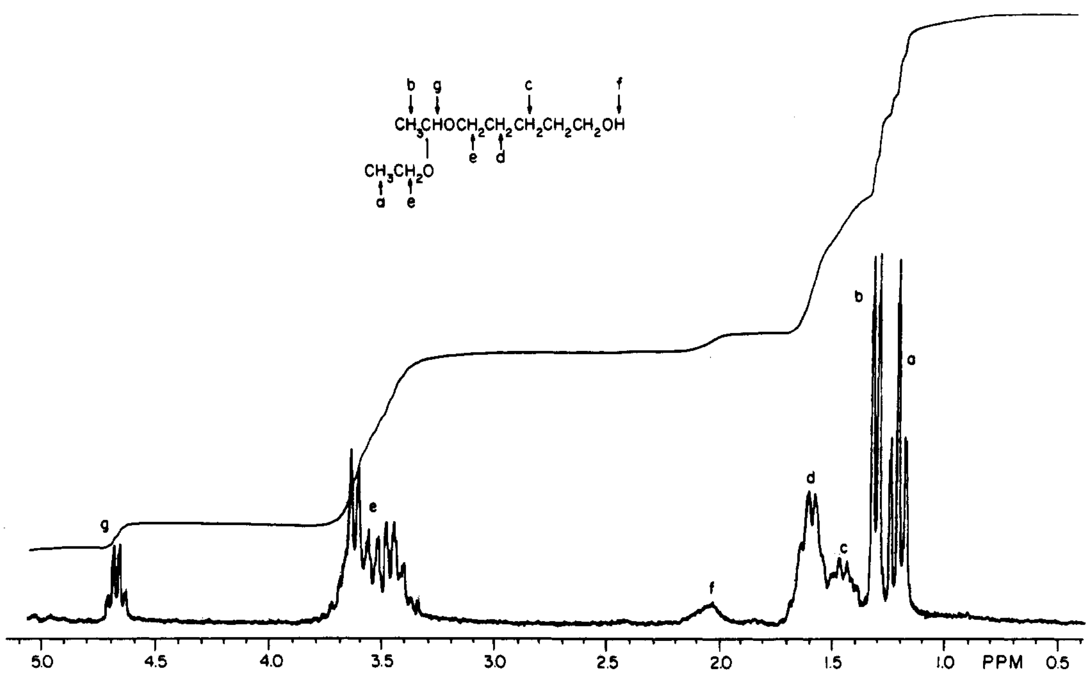


Figure 5. 200-MHz ^{13}C NMR spectrum of masked acetal/alcohol 3 in $CDCl_3$ at 25 °C.

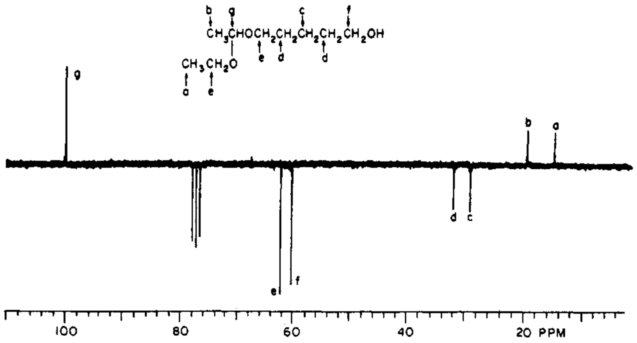
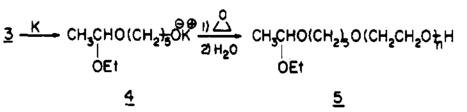


Figure 6. 50-MHz ^{13}C NMR spectrum of masked acetal/alcohol 3 using attached proton test sequence (CH, CH_3 pos; CH_2, C neg) in $CDCl_3$ at 25 °C.



$$\mathbf{3} \xrightarrow{K} \underset{OEt}{CH_3CHO}(CH_2)_5O^{\ominus}K^{\oplus} \xrightarrow[2)\,H_2O]{1)\,\overset{O}{\triangle}} \underset{OEt}{CH_3CHO}(CH_2)_5O(CH_2CH_2O)_nH$$

4 **5**

Figure 7. Polymerization of ethylene oxide with the masked acetal alkoxide initiator 4.

Anionic Polymerization of Ethylene Oxide with Masked Initiator 4. The reaction of 3 with potassium gives the alkoxide initiator 4, and this initiator effectively polymerizes ethylene oxide, yielding 5 (Figure 7). It is essential that the acetal end group shown in structure 5 actually be present; otherwise, further reactions to create the desired telechelomer would be fruitless. The 300-MHz ^{1}H NMR spectrum, presented in Figure 8, unequivocally shows the acetal mask is still present. The triplet at 1.2 ppm and the doublet at 1.3 ppm represent the methyls of the acetal, and the quartet at 4.7 ppm represents the methine proton. The "c" and "d" protons in the initiator are also seen in this spectrum; while the c protons appear around 1.4 ppm, "d" protons appear to 1.6 ppm. The major signal at 3.6 ppm is due to protons of the ethylene oxide repeat units.

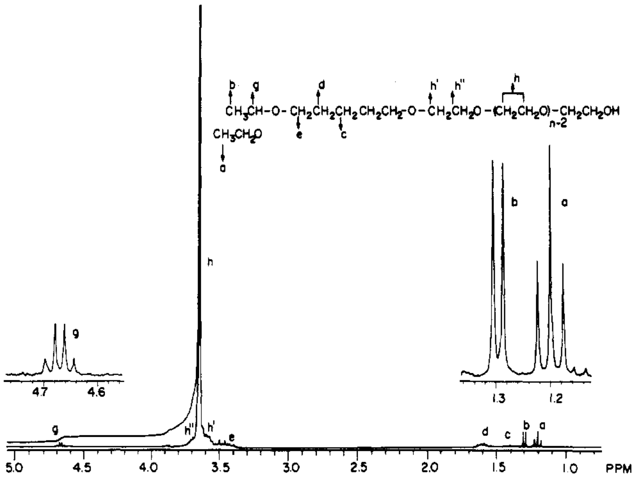


Figure 8. 300-MHz ^{1}H NMR spectrum of masked polyether 5 in $CDCl_3$ at 25 °C.

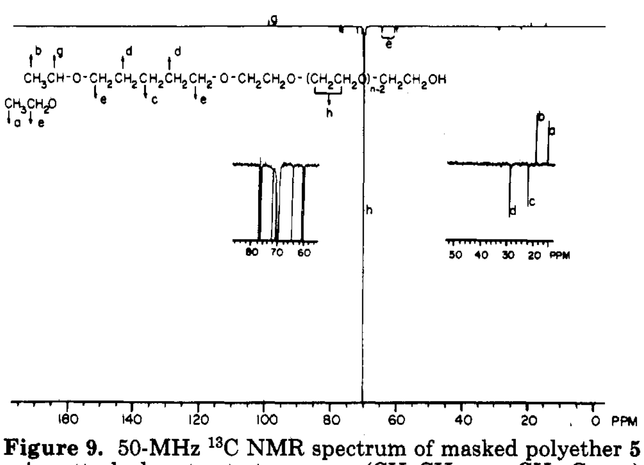
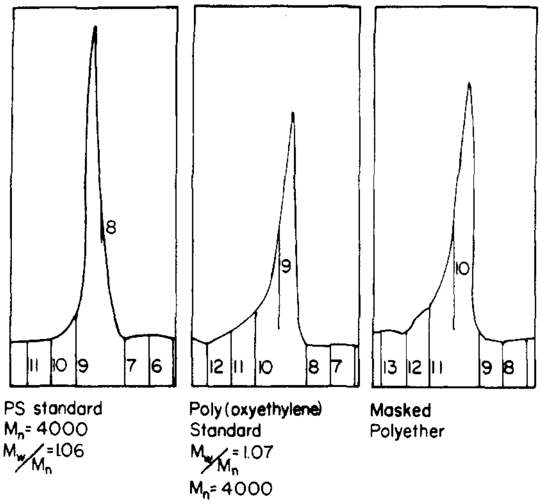


Figure 9. 50-MHz ^{13}C NMR spectrum of masked polyether 5 using attached proton test sequence (CH, CH_3, pos; CH_2, C, neg) in $CDCl_3$ at 25 °C.

The ^{13}C NMR APT spectrum confirms the proton assignments (Figure 9). The presence of the initiator moiety is evident from the signals "g", "a", and "b" appearing at 98.9, 14.8, and 19.3 ppm, which correspond to methine and the two different methyl carbons in the acetal mask. The carbons in the EO units give a major signal "h" at 69.9 ppm



PS standard
M_n = 4000
M_w/M_n = 1.06

Poly(oxyethylene) Standard
M_w/M_n = 1.07
M_n = 4000

Masked Polyether

Figure 10. Gel permeation chromatographs in CH_2Cl_2 at 25 °C: flow rate, 1 mL/min; column, 10^3 Å μStyragel.

with small signals nearby, which could be assigned to end EO units. The "e" methylene carbons attached to ether oxygens appearing between 60.1 and 64.5 ppm also come from the initiator moiety.

Gel permeation chromatographs (GPC) show that **5** has a narrow molecular weight distribution (Figure 10). Also shown in the figure are the GPC curves of a polystyrene standard and a poly(oxyethylene) standard having narrow molecular distributions. It is clearly evident that **5** has a narrow molecular weight distribution. Some absorptive effects are seen in both the poly(oxyethylene) standard and **5**; such effects have been observed before. The number-average molecular weight of **5** given in Figure 10 was calculated by using 300-MHz ^{1}H NMR; sufficient relaxation times were given to obtain a fairly accurate integration.

This research is continuing with the subsequent addition of a pivalolactone segment to form the telechelomer to be followed by step propagation to form highly regular segmented copolymers that should be capable of excellent phase separation.

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Registry No. **1**, 30502-4-1; **2**, 37494-03-4; **3**, 107576-73-8; **4**, 104066-38-8; **5**, 102773-45-5; (EO)(PVL) (block copolymer), 107558-01-0; $Cl(CH_2)_3OH$, 627-30-5; $EtOCH{=}CH_2$, 109-92-2; ethylene oxide, 75-21-8.

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Chain Orientation in Highly Drawn Polystyrene

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A recent small-angle neutron scattering (SANS) study,[1] using substantially monodisperse atactic polystyrene of $M_w = 6 \times 10^5$ doped with 5% deuteriated polymer ($M_w = 5.5 \times 10^5$), has shown that the axial strain represented by the deforming molecular envelope is affine with the applied strain for deformation at 127 °C. Data from this work are replotted in Figure 1 as the spherical harmonic $\langle P_2 \rangle$, which describes the orientation function of vectors orienting affinely with the molecular envelope against the macroscopic draw ratio. These vectors can be identified with network displacement vectors.

The recently developed methods of assessing molecular orientation from wide-angle X-ray scattering (WAXS)[2] can provide a reasonable direct quantitative measure of the orientation of statistical chain segments. Application of this technique to the highly drawn polystyrene produced the slightly surprising result that, even though some of the draw ratios were probably the highest ever obtained with this polymer, the segmental orientation was so low as to be only just detectable. The P_2 coefficients defining the segmental orientation were calculated from the azimuthal distribution of the equatorial scattering maximum at $2\theta = 10°$ (Cu Kα). No correction was made for the intrinsic azimuthal width of this peak, and in view of the low orientations encountered, the errors will be small. The WAXS measurements of segmental orientation are plotted as full circles in Figure 1. Such gradual segmental orientation with strain would be the expected behavior of chains with a large number of links between network points.[3] Curves calculated by using Treloar's approximate expression[4] for chains with 100, 200, and 500 statistical chain segments are also drawn as the broken lines. The behavior can thus be understood if chain lengths between cross-link points are of this order. The degree of polymerization of the molecules, around 5000, is obviously sufficient, although the critical factor is the scale of the effective network. Recent measurements of the entanglement molecular weight using narrow fractions of polystyrene[5] give a value of 18×10^3 or 173 monomer units. It should be noted that in the glassy phase below T_g, noncrystalline polymers show a much more rapid development of orientation with strain especially at low strains (e.g., ref 6).

This experiment demonstrates that even at high levels of chain extension, the degree of segmental orientation may remain low if the effective network length is large. However, the apparent network length depends very significantly on the conditions of deformation as well as the strain.[7]

Note on Calculations of $\langle P_2 \rangle$ from the SANS Data

For each external λ, the SANS λ_N was found from ref 1.