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C. T. Imrie[a]; F. E. Karasz[b]; G. S. Attard[c]
[a] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, USA [b] Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Scotland [c] Department of Chemistry, University of Southampton, Southampton, England

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THE EFFECT OF MOLECULAR WEIGHT ON THE THERMAL PROPERTIES OF POLYSTYRENE-BASED SIDECHAIN LIQUID-CRYSTALLINE POLYMERS

C. T. IMRIE† and F. E. KARASZ*

Department of Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003, USA

G. S. ATTARD

Department of Chemistry
University of Southampton
Southampton SO9 5NH, England

ABSTRACT

Sidechain liquid-crystalline polymers were prepared by the derivatization of three poly(4-hydroxystyrene) fractions of different molecular weights ($M_w = 1.0 \times 10^4$, 2.2×10^4, and 3.0×10^4). 4-Cyanoazobenzene and 4-cyanobiphenyl were incorporated as mesogenic groups with ether-linked methylene spacers of varying length. The polymers all exhibited a smectic A phase, with the exception of the propyl member of the cyanobiphenyl series for which no liquid-crystalline behavior was observed. For short spacers the thermal properties were insensitive to molecular weight changes in the backbone, whereas small but consistent differences in the transition temperatures and entropies were observed as the number of methylene groups in the spacer increased.

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†Permanent address: Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland.

INTRODUCTION

Sidechain liquid-crystalline polymers have generated interest in recent years because they exhibit a unique duality of properties combining ease of processibility and glassy behavior with the electrooptic properties of low molar mass mesogens [1]. In consequence, this class of materials has application potential in the area of advanced electrooptic technologies including, for example, optical information storage [2] and nonlinear optics [3]. In addition, these polymers are of fundamental interest because the polymer configurational entropy appears to be antagonistic to liquid-crystalline order. A sidechain liquid-crystalline polymer comprises three structural components: a polymer backbone, a pendant mesogenic group, and a flexible alkyl spacer. Such a material offers the molecular engineer a high degree of control over the thermal, optical, and dielectric properties of the system. However, to capitalize on this richness of structure, an understanding of structure–property relationships is prerequisite to the rational design of new materials with targeted functionality and performance. To derive such knowledge, it is necessary to compare the properties of different backbones. In making such comparisons, however, the effect of the molecular weight of the polymer on its mesogenic characteristics must also be considered.

As part of a continuing program to develop new materials for advanced electrooptic technologies, we have undertaken a systematic investigation into structure-property relationships in sidechain liquid-crystalline polymers derived from polystyrene [4–7]. In this contribution we compare the properties of polystyrene-based polymers prepared by derivatizing three backbones of differing molecular weight, namely, $M_w = 1.0 \times 10^4$, 2.2×10^4, and 3.0×10^4, with nominal degrees of polymerizations of 80, 180, and 250, respectively. The structures of the polymers investigated are shown in Fig. 1.

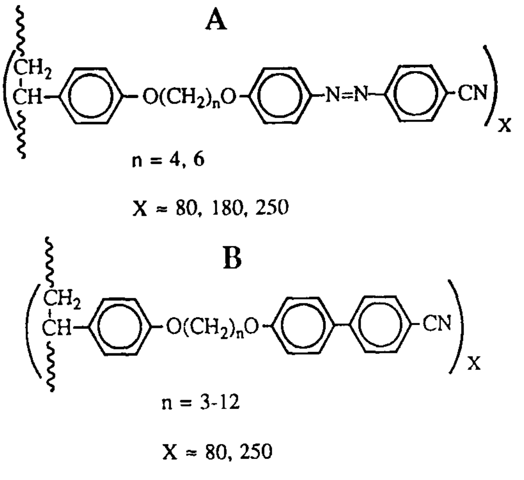


FIG. 1. Structures of cyanoazobenzene-substituted (A) and cyanobiphenyl-substituted (B) polymers.

The effect of molecular weight (M) on the glass transition temperature T_g is usually expressed in terms of a simple reciprocal relationship, i.e., $T_g(M) = T_g(\infty) - kM^{-1}$, where $T_g(\infty)$ is the asymptotic value for infinite molecular weight polymer and k is a constant which, for flexible chain polymers, is typically of the order of 10^3-10^4. The molecular-weight dependence for other types of transitions in liquid-crystal polymer is more controversial (see discussion below), and this provides a certain motivation for the present study.

An understanding of molecular weight effects is particularly relevant in the development of this class of materials for it is clear that polymers designed for specialty applications must have a reproducible performance level from one synthetic batch to another. Undoubtedly, this will be determined to some extent by the molecular weight and polydispersity of the polymers.

EXPERIMENTAL

Synthesis

The synthetic route for the cyanoazobenzene-substituted polymers is shown in Fig. 2. The scheme for the cyanophenyl-substituted polymers is analogous to that shown. The coupling of a diazotized 4-substituted aniline with phenol is described elsewhere [8]. The synthesis of both monomers and polymers is now well documented in the literature [7, 9, 10]. Poly(4-hydroxystyrene)s of various molecular weights were obtained from Polysciences, Inc. The purification of the derivatized polymers involved a single precipitation followed by exhaustive Soxhlet extraction with methanol. The extraction of excess sidechain was monitored by using thin-layer

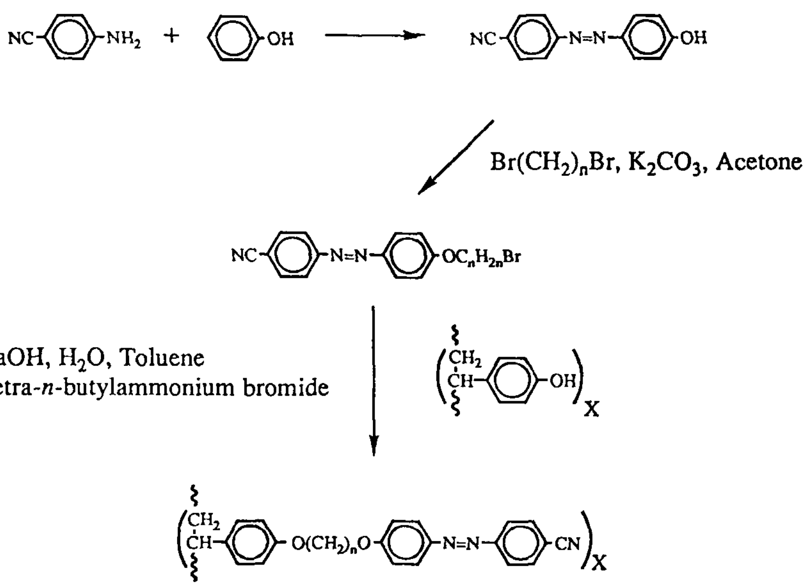


FIG. 2. Scheme for the synthesis of cyanoazobenzene-substituted polymers.

TABLE 1. Elemental Analyses of the Cyanozobenzene-Substituted Polymers

				C		H		N	
n	$M_w \times 10^4$[a]	Formula	Mol. wt.	Calc.	Found	Calc.	Found	Calc.	Found
4	1.0	$(C_{25}H_{23}N_3O_2)_m$	$(397.5)_m$	75.54	75.33	5.83	5.81	10.57	10.66
4	2.2	$(C_{25}H_{23}N_3O_2)_m$	$(397.5)_m$	75.54	74.99	5.83	5.89	10.57	10.62
4	3.0	$(C_{25}H_{23}N_3O_2)_m$	$(397.5)_m$	75.54	75.11	5.83	5.87	10.57	10.63
6	1.0	$(C_{27}H_{27}N_3O_2)_m$	$(425.5)_m$	76.21	75.65	6.40	6.29	9.88	9.58
6	2.2	$(C_{27}H_{27}N_3O_2)_m$	$(425.5)_m$	76.21	75.82	6.40	6.19	9.88	9.78
6	3.0	$(C_{27}H_{27}N_3O_2)_m$	$(425.5)_m$	76.21	75.84	6.40	6.14	9.88	9.71

[a] Refers to the poly(4-hydroxystyrene) used in the reaction.

chromatography and verified by elemental analyses, which are listed in Tables 1 and 2 for the cyanoazobenzene-substituted and the cyanobiphenyl-substituted polymers, respectively. The degree of backbone coverage was considered to be 100% complete within our experimental detection limits; as we have shown elsewhere, IR spectroscopy is particularly useful in determining this parameter [6]. Characteristic spectra for both the monomers and polymers have been given elsewhere [11]. The synthetic methods used have been shown to produce derivatized polymers with unchanged degrees of polymerization; polydispersities are also unaffected [6, 11].

Characterization

The structures of all the polymers and their intermediates were verified by ^{1}H-NMR spectroscopy using a Varian XL200 NMR spectrometer; by FTIR spectroscopy using an IBM System 9000 FTIR spectrometer; and by elemental analysis

TABLE 2. Elemental Analyses of the Cyanobiphenyl-Substituted Polymers Derived from Poly(4-hydroxystyrene), $M_w = 1.0 \times 10^4$

			C		H		N	
n	Formula	Mol. wt.	Calc.	Found	Calc.	Found	Calc.	Found
3	$(C_{24}H_{21}NO_2)_m$	$(355.4)_m$	81.10	80.22	5.96	5.90	3.94	3.84
5	$(C_{26}H_{25}NO_2)_m$	$(383.5)_m$	81.43	81.18	6.57	6.58	3.65	3.66
6	$(C_{27}H_{27}NO_2)_m$	$(397.5)_m$	81.58	81.08	6.85	6.91	3.52	3.53
7	$(C_{28}H_{29}NO_2)_m$	$(411.5)_m$	81.72	80.98	7.10	7.02	3.40	3.39
8	$(C_{29}H_{31}NO_2)_m$	$(425.5)_m$	81.85	81.08	7.34	7.32	3.29	3.25
9	$(C_{30}H_{33}NO_2)_m$	$(439.6)_m$	81.97	81.30	7.57	7.58	3.19	3.17
10	$(C_{31}H_{35}NO_2)_m$	$(453.6)_m$	82.08	82.52	7.78	7.76	3.09	3.15
11	$(C_{32}H_{37}NO_2)_m$	$(467.6)_m$	82.19	81.63	7.98	8.20	3.00	2.89
12	$(C_{33}H_{39}NO_2)_m$	$(481.6)_m$	82.29	81.98	8.16	8.01	2.91	2.87

TABLE 3. Transitional Properties of the Cyanoazobenzene-Substituted Polymers

n	$M_w \times 10^{4\,a}$	T_g/°C	T_{CI}/°C	ΔH/J·g^{-1}	$\Delta S/R$
4	1.0	86	161	3.94	0.43
4	2.2	87	165	3.94	0.43
4	3.0	89	165	3.88	0.42
6	1.0	72	164	6.46	0.76
6	2.2	73	168	5.71	0.66
6	3.0	74	170	5.43	0.63

[a]Refers to the poly(4-hydroxystyrene) used in the reaction.

performed by the University of Massachusetts Microanalytical Laboratory. The phase behavior of the polymers was investigated with a Zeiss polarizing microscope equipped with a Linkam hot stage. In addition, the materials were characterized further by differential scanning calorimetry using a Perkin-Elmer DSC-7 differential scanning calorimeter. The liquid crystal–isotropic transition temperatures quoted correspond to the peak maximum temperatures, and the glass transition temperatures correspond to the inflection in the baseline. The heating and cooling rates in all cases were 10°C·min^{-1}.

RESULTS AND DISCUSSION

The thermal properties of the polymers are listed in Tables 3 and 4. With the sole exception of the propyl member of the cyanobiphenyl series, all the polymers

TABLE 4. Transitional Properties of the Cyanobiphenyl-Substituted Polymers Derived from Poly(4-hydroxystyrene), $M_w = 1.0 \times 10^4$

n	T_g/°C	T_{CI}/°C	ΔH/J·g^{-1}	ΔS/R
3	78	–	–	–
4	75	105	1.00	0.12
5	60	102	2.96	0.36
6	61	117	4.76	0.58
7	42	111	4.78	0.62
8	36	121	6.67	0.87
9	29	115	5.27	0.72
10	17	119	8.53	1.19
11	13	114	9.39	1.37
12	13	113	6.44	1.03

exhibit liquid-crystalline behavior. Differential scanning calorimetry revealed two transitions for these materials: a second-order transition corresponding to the glass transition and a weak first-order transition, the liquid crystal-isotropic transition. Polarizing light microscopy was used to identify the mesophase. To obtain an optical texture for phase identification, the polymer was heated about 10°C above its clearing point and allowed to cool slowly, typically at the rate of 0.2°C$\cdot$min^{-1}, into the mesophase. This method allowed bâtonnets to develop at the transition; on further cooling, these structures coalesced to form a focal conic fan texture, which typically implies the presence of a layered molecular structure. In addition, regions of homeotropic texture were observed, a result indicating that the director of the phase is orthogonal with respect to the layer planes. Thus, the phase was assigned as a smectic A. This view has been supported by x-ray diffraction studies of the butyl members of the polymers derived from the poly(4-hydroxystyrene), $M_w = 1.0 \times 10^4$. These experiments revealed, specifically, the presence of an interdigitated smectic A phase [11].

4-Cyanoazobenzene-Substituted Polymers

The thermal properties of the cyanoazobenzene-substituted polymers are listed in Table 3. As molecular weight increases, the glass transition temperatures increase, although the differences are small and of a magnitude comparable to experimental error. By comparison, the differences in the clearing temperatures are somewhat larger, a result suggesting a small but real increase in the smectic–isotropic transition temperature as the average molecular weight of the polymer backbone increases. The entropy associated with the clearing transition, quoted as the dimensionless quantity $\Delta S/R$, appears to be insensitive within our experimental limits to the changes in the degree of polymerization. Crivello et al. [9] have prepared the butyl and the hexyl homologues of this polymer series, and the two sets of data show good agreement [12]. We have discussed the differences in the phase assignments elsewhere [11]. Although Crivello et al. identified these polymers as nematogens, our studies using x-ray diffraction and polarizing light microscopy unambiguously show smectic behavior.

4-Cyanobiphenyl-Substituted Polymers

Table 4 lists the thermal properties of the cyanobiphenyl-substituted polymers derived from the backbone with $M_w = 1.0 \times 10^4$. The properties of polymers derived from poly(4-hydroxystyrene), $M_w = 3.0 \times 10^4$, have been reported elsewhere [13].

Figure 3 compares the glass transition temperatures and the clearing points for the two series. It is immediately apparent that the differences between the two sets of data are again small and, in particular, the T_gs are within or close to experimental error. The glass transition temperature falls as the number of methylene groups in the alkyl spacer increases. This result is presumably a consequence of the

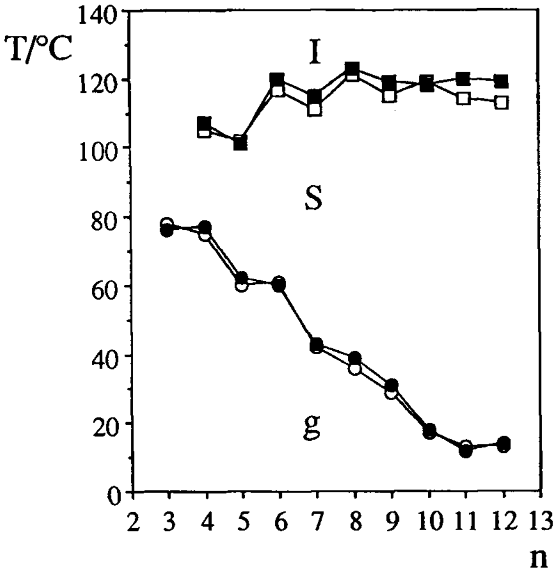


FIG. 3. Dependence of the transition temperatures on the number of methylene groups in the alkyl spacer for the cyanobiphenyl-substituted polymers. Glass transition temperatures are denoted by circles and the clearing points by squares. Open symbols denote the polymers with $M_w = 1.0 \times 10^4$ backbone; filled symbols indicate the polymers with $M_w = 3.0 \times 10^4$ backbone. G, glassy phase; I, isotropic phase; S, smectic phase.

plasticization effect of the sidechain. A small odd-even effect is exhibited by the glass transition temperatures on increasing the spacer length. Although this effect has been observed for other polystyrene-based sidechain polymers [14], its molecular significance is speculative.

The clearing temperatures for both sets of polymers also exhibit a small odd-even effect as the number of methylene groups in the spacer increases. For the majority of the cases the smectic-isotropic transition temperatures of the higher molecular weight polymers are slightly higher, although this effect is again small. These differences appear to be more pronounced as the number of methylene groups in the spacer increases.

Figure 4 compares the entropy change associated with the clearing points for these polymers. For low members of the series, the entropies of transition are similar. As the spacer length increases, however, the differences in the two sets of data become appreciable. The dependence of $\Delta S/R$ on the spacer length for the polymers based on the 1.0×10^4 backbone is clearly less regular than that of the higher molecular weight polymers. In general, however, both sets of data show an increasing trend in $\Delta S/R$ as spacer length increases. This trend presumably reflects increases in the translational, conformational, and orientational contribution to the entropy of transition.

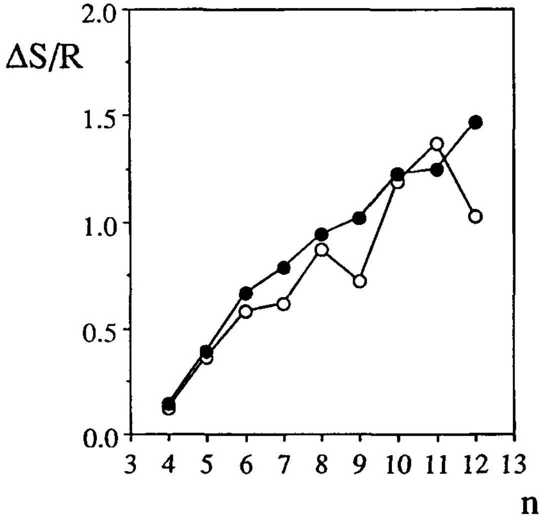
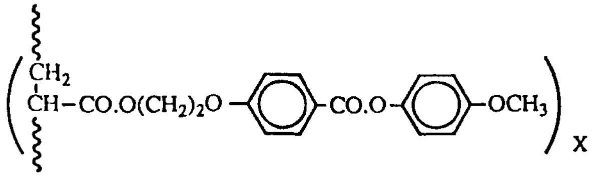


FIG. 4. Dependence of the entropy associated with the smectic–isotropic transition on the number of methylene groups in the alkyl spacer for the cyanobiphenyl-substituted polymers. (○) polymers with $M_w = 1.0 \times 10^4$ backbone; (●) polymers with $M_w = 3.0 \times 10^4$ backbone.

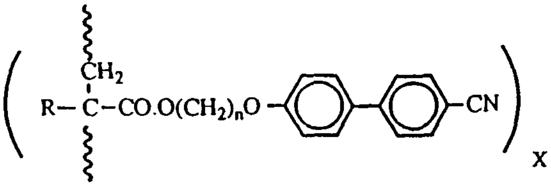
Comparisons with Other Backbones

The effects of molecular weight on the properties of sidechain liquid-crystalline polymers have now been investigated for a range of polymer backbones [15, 16], and it is instructive to place our data for polystyrene-based sidechain polymers in the context of these other studies. Portugall et al. [17] showed that for a polyacrylate-based polymer (Structure I), T_{NI} increased from 114 to 116°C as the DP of the polymer increased from 41 to 114, and $\Delta S_{NI}/R$ increased from 0.19 to 0.28. It is important to note that these are changes that may still lie within experimental error.



STRUCTURE I.

The results of Portugall et al. differ quantitatively from Kostromin et al. [18], who performed a more detailed study of polyacrylate- and polymethacrylate-based polymers (Structure II). Kostromin et al. found that a sharp increase in T_{CI} was observed up to DP ≈ 240, at which point a molecular-weight-independent regime was found. We note that in this study the molecular weights were derived from intrinsic viscosity data.

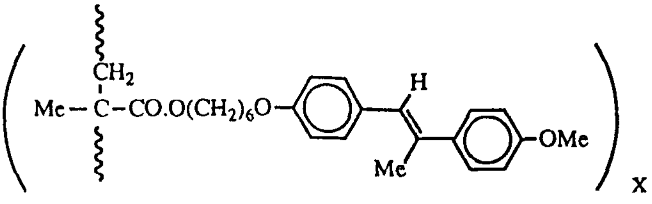


n = 5, 11

R = H, CH_3

STRUCTURE II.

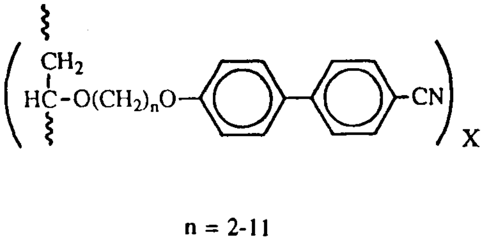
A similar dependence was not found by Percec et al. [19] for the polymer shown in Structure III, for which T_g and T_{NI} increased as DP increased only up to the surprisingly low value DP ≈ 10–12. The enthalpy change for the liquid-crystalline transition was found to be essentially molecular weight independent.



STRUCTURE III.

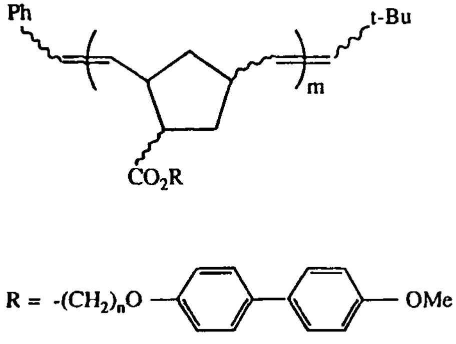
For the polysiloxane-based mesogenic polymers, Stevens et al. [20] showed that, up to DP ≈ 10, both T_g and T_{CI} increased rapidly as DP increased. Subsequent increases in DP resulted in little change in these temperatures. In particular, T_{SI} was insensitive to changes in molecular weight above DP ≈ 10. These results were not supported by the findings of Gray [16], who reported that T_g increased as DP increased up to DP ≈ 75, after which point only small increases were observed upon further increases in the molecular weight. The T_{NI} increased less quickly as DP increased but also leveled off less quickly, whereas the T_{SI} showed behavior similar to the T_g although the dependence was not as strong.

The most comprehensive study to date of the effects of variation in molecular weight has been undertaken by Percec et al. [21–25] using the poly{ω-[(4-cyano-4′-biphenyl)oxy]alkyl vinyl ether}s (Structure IV).



STRUCTURE IV.

This family of polymers may be synthesized by living cationic polymerization, and therefore are of well-defined molecular weight with narrow molecular weight distributions. In these studies, however, the maximum available values of the DP have been near 30, and in this range the mesogenic properties of the polymers may still lie within the molecular weight-dependent regime. Heroguez et al. [26], in another study of the same system, showed that the properties of the hexyl member of this polymer series with DP ≈ 37 and 55 were essentially the same. In addition, Jonsson et al. [27] prepared the decyl member of this series with DP ≈ 107. This polymer had a T_{SI} just 2°C higher than that reported by Percec et al. [22] for the polymer with DP ≈ 28. Komiya et al. [28, 29] prepared mesogenic sidechain polymers by ring-opening metathesis polymerization (Structure V). These studies suggest that the glass transition and clearing temperatures become independent of molecular weight at approximately 30–50 repeat units. This was found to be the case also for a group of closely related polymers having cyanobiphenyl as the mesogen [30].



STRUCTURE V.

Even this brief overview of the dependence of the thermal properties of sidechain liquid-crystalline polymers on molecular weight has revealed contradictory evidence. However, the general trend that emerges from all these examples is that increasing DP results, initially, in increased transition temperatures but that at some point further increases in DP have little or no effect. Stevens et al. [20] proposed that this may be understood in terms of the specific free volume of the system and its dependence on DP. According to this model, an initial increase in DP reduces the free volume and leads to a closer packing of the mesogenic side groups. This packing effect accounts for the initial rise in both the glass transition temperature and the clearing temperature. The conventional view of the increase in T_g with molecular weight is, of course, in terms of the "extra" free volume contributions associated with polymer chain ends; the fractional decrease in this contribution with increasing DP leads directly to the well-known reciprocal relationship mentioned above. An analogous explanation could in principle be invoked to account for mesogenic transition behavior. The slight increase in the backbone molecular weight dependence noted in Fig. 3 for longer spacer groups suggests that the contributions to the total free volume in any transition temperature vs DP relationship should include terms which originate in the side group. A definitive examination of these effects will require polymers with well-defined spacer groups and a range of molecular weights.

The agreement between our data and that of Crivello et al. [9], who used backbones from a different source, shows that it is possible to obtain polymers with well-defined properties without having to resort to laborious fractionation techniques. This achievement is clearly important in the technological development of this class of materials. Finally, we note that in many respects polystyrene-based polymers behave in a fashion similar to that of polysiloxane-based materials [16], a similarity suggesting that the flexibility of the polymer backbone does not influence the dependence of the thermal properties on molecular weight.

ACKNOWLEDGMENT

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