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Notes

Glass Transition Temperatures of Polymethacrylates with Alicyclic Side Groups

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Introduction

The presence of long flexible *n*-alkyl substituents has a profound impact on the glass transition temperature T_g of various classes of macromolecules, including polyolefins,[1,2] poly(*p*-alkylstyrenes),[3] polyacrylates,[4] and polymethacrylates.[4,5] As the length of the *n*-alkyl side chain increases, T_g decreases within each of these families of polymers.

The effect of varying the size of alicyclic ring substituents on T_g has not, with one exception, been explored. Wilson and Simha[6] previously determined the T_g's of poly(cyclohexyl methacrylate) and poly(cyclopentyl methacrylate) by volume expansion. In this note we report T_g for a series of six fractionated high molecular weight polymethacrylates with ring sizes ranging from cyclo butyl to cycloheptadecyl.

Experimental Section

Monomers and polymers were synthesized by methods that were reported previously.[7] The polymers were fractionated by addition of methanol to dilute toluene solutions (<1% w/w). Molecular weights and polydispersities were obtained by low-angle laser light scattering (LALLS), osmometry, and size exclusion chromatography (SEC), as previously described.[7] Molecular characteristics of the selected fractions are presented in Table I.

Tacticities were determined by ^{13}C NMR measurements in $CDCl_3$ at 25 °C. The triad concentrations were evaluated from the intensities of peaks corresponding to the carbonyl carbon.

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to measure T_g. Calibration of this instrument was based on an indium standard. Sample sizes of 5–10 mg and a heating rate of 5 °C min^{-1} were employed.

Results and Discussion

Table II lists the tacticities and glass transition temperatures of the polymethacrylates. For materials prepared under identical conditions (AIBN initiation, 50 °C), the tacticity is independent of the size of the alicyclic side group.

Table I
Molecular Weights and Polydispersities of Fractionated Polymethacrylates

polymer	$10^{-4}\bar{M}_{\mathrm{w}}$[g]	$10^{-4}\bar{M}_{\mathrm{n}}$[h]	$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$[i]	$\bar{M}_z/\bar{M}_{\mathrm{w}}$[i]
PCBM[a]	13.9	12.1	1.3	1.3
PCPM[b]	11.0	10.4	1.2	1.2
PCOM[c]	12.1	9.1	1.4	1.3
PCDM[d]		33.4[j]	1.7	1.6
PCDDM[e]	9.8	7.3	1.4	1.5
PCHDM[f]		12.2[j]	1.6	1.4

[a] Poly(cyclobutyl methacrylate). [b] Poly(cyclopentyl methacrylate). [c] Poly(cyclooctyl methacrylate). [d] Poly(cyclodecyl methacrylate). [e] Poly(cyclododecyl methacrylate). [f] Poly(cycloheptadecyl methacrylate). [g] LALLS. [h] Osmometry. [i] SEC. [j] Via SEC based on a polystyrene calibration.

Table II
Tacticity and Glass Transition Temperatures of Polymethacrylates

		tacticity, %		
polymer	T_g, °C	mm	mr + rm	rr
PCBM	78	3	32	65
PCPM	75	2	32	66
PCOM	73	3	34	63
PCDM	58	3	30	67
PCDDM	56	3	34	63
PCHDM	56	2	31	67

On the other hand, T_g is affected by ring size. As the alicyclic ring becomes larger, T_g decreases from the value of 78 °C found for PCBM and then appears to level off (at 56 °C) for the largest rings investigated (C_{12} and C_{17}). A plot of T_g versus the number of carbons in the side group is presented in Figure 1 for both alicyclic and *n*-alkyl-substituted polymethacrylates. The impact on T_g of increasing ring size is quite modest compared to the very large decreases observed with *n*-alkyl substituents with the same number of carbons.

T_g is known to increase with an increase in substituent size for rigid substituents because of the increased barrier to rotation about backbone bonds.[8,9] However, for flexible side chains such as *n*-alkyl, only the first methylene group is attached rigidly to the methacrylate backbone. The remainder of *n*-alkyl chains can avoid rotating backbone units; thus the addition of these groups has the effect of decreasing T_g ("internal plasticization").[8,9] Although alicyclic side groups are not rigid, their cyclic structure moves the center of mass of the side group closer to the polymer backbone and the bulkiness of the substituent becomes important with regard to T_g. The ali-

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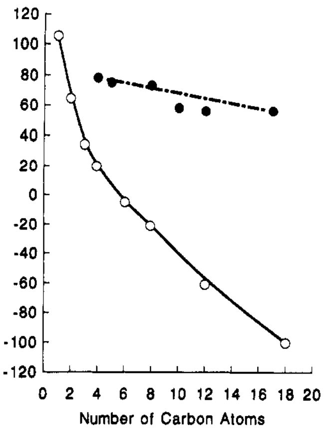

Figure 1. T_g versus number of carbon atoms in the *n*-alkyl (○) or alicyclic (●) side group. Data for T_g of poly(*n*-alkyl methacrylates) are taken from ref 9. The dashed line for the ring materials and the solid curve for the *n*-alkyl materials are intended to guide the eye; i.e., they are not statistical fits to the data.

cyclic rings also are less flexible (have fewer conformations available to them) than the corresponding *n*-alkyl derivatives. Furthermore, the carbon linked to the carbonyl for alicyclic polymethacrylates may be viewed as disubstituted. It is interesting, therefore, to compare the T_g of PCBM (78 °C) with that of poly(*sec*-butyl methacrylate) (T_g = 60 °C[10]), which has the same degree of substitution. The *sec*-butyl group is bulkier than the cyclobutyl ring, but the latter is more rigid and thus imparts the higher T_g. On going to the bulky and rigid ("trisubstituted") *tert*-butyl group, a still higher T_g of 118 °C[10] is found.

In summary, the effects of both internal plasticization and bulkiness of the ring appear to influence the T_g of alicyclic polymethacrylates. The observed slight decrease of T_g with ring size shows that these two effects roughly offset one another for the polymethacrylates of this work.

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Registry No. PCBM, 118420-90-9; PCPM, 28298-90-0; PCOM, 28298-92-2; PCDM, 64328-83-2; PCDDM, 64328-84-3; PCHDM, 127333-31-7.

Oxygen Enrichment by a Langmuir–Blodgett Film of Poly(*N*-dodecylacrylamide) on Porous Aluminum Oxide

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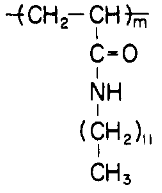
Introduction

The development of permselective membranes is important for the establishment of energy-saving processes. It is well-known that the Langmuir–Blodgett (LB) technique provides uniform ultrathin films with well-defined molecular orientation.[1,2] The use of LB multilayers for gas separation has been desired, but there have been only a few studies: Rose and Quinn,[3] Gaines and Ward,[4] and Albrecht et al.[5] have measured gas permeability through LB films such as barium stearate and cadmium arachidate. They found only a decrease in gas flux by the LB films. Effective gas separation was not achieved. Higashi et al. have reported the selective permeation of oxygen by LB films consisting of fluorocarbon amphiphiles.[6,7]

Some of the present authors[8-12] have recently shown that *N*-alkyl-substituted acrylamides and preformed poly(*N*-dodecylacrylamide) give stable uniform LB multilayers. We have attempted to use these polymer LB films for separation processes. In this note, it is demonstrated that the LB film of poly(*N*-dodecylacrylamide) (PDDA (1)) deposited on a porous aluminum oxide acts as a permselective membrane for oxygen.



$$-\!\!\left(CH_2-\underset{\substack{|\\ C=O\\ |\\ NH\\ |\\ (CH_2)_{11}\\ |\\ CH_3}}{CH}\right)\!\!_{\overline{m}}$$

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