Polymer Bulletin 24, 405–411 (1990)

Polymer Bulletin

New models for the prediction of the relaxation behavior of vinyl polymers with bulky side groups and α-methyl groups in the primary transition region

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Summary

Modified models for the prediction of the slope index of the viscoelastic master curve in the primary transition region for vinyl polymers with either bulky side groups or α-methyl groups have been proposed. Very good agreeements between predicted and experimental values are found. The modified models take into account of the effect of the bulky side group or α-methyl groups in the contribution to the corrected number of the main-chain atoms. The predicted slope index was found to be proportional to (i) the average cohesive energy per main-chain atom; U/N, which represents the enthalpic interchain interaction, (ii) the entropic intrachain interaction as defined by H/N, and (iii) the average spatial molecular volume per main-chain atom V/N .

Introduction

Previous communication has reported a new model for the predicton of the relaxation behavior of vinyl polymers in the primary transition region using functional group additive properties of fundamental molecular parameters (1).Excellent agreements between predicted and experimental values have been obtained for vinyl type polymers without bulky side group.

When the model was applied to vinyl polymers with bulky side groups (e.g. poly-2 ethyl-hexyl acrylate) or polymers with α– methyl group (e.g. poly-methyl methacrylate), the predicted values are much higher than those experimentally observed. The purpose of this paper is to rationalize the discrepancies and to demonstrate how the slope-index model can be modified to accommodate vinyl polymers with bulky side groups as well as α– methyl groups so as to allow accurate prediction of their slope indices.

Experimental

The poly(methyl methacrylate) and poly(α– methyl styrene) samples were purchased from Polysciences, Inc. The five polyacrylates with bulky side-groups , namely poly(iso-butyl acrylate), poly(3,3 dimethyl butyl acrylate), poly(iso-octyl acrylate), poly(2-ethyl hexyl acrylate) and poly(iso-decyl acrylate) were solution polymerized in ethyl acetate at 80°C using AIBN (Vazo-64) as the initiator. The number average molecular weight M_n and the dispersity indices M_w/M_n as determined by GPC are respectively 23000 and 6.5, 240000 and 6.4, 31000 and 6.5, 42000 and 4.8 and 19000 and 8.3 .

Dynamic mechanical measurements were carried out on a Rheometrics dynamic spectrometer (RDS-7700) using wither 8-mm parallel plates or torsional fixtures. Very good agreeement has been found between these two modes of measurement. Master curves were constructed from the frequency sweep data at different temperatures using the horizontal shift only. Good superposition of the data were observed with all the samples studied. The SIs of the G'(ω) master curves have been reported to be in good agreement with the SIs of the stress-relaxation master curves (6,7).

Results and Discussions

1)Description of the original Slope-Index Model

The original slope-index model used functional group properties which are defined as follows:

U is the cohesive energy per group
H is the group contribution to the internal rotational degree of freedom
N is the number of main-chain atoms per group
V is the group contribution to molar volume

For vinyl polymers, N is equal to 2. The values of U and H used are those originally published by Hayes (2), while the values of V are based on Lebas's report of atomic molar volume as reviewed by Kaeble. (3). The method of calculating U, H and V for polymers have been reported elsewhere (4).

It has been shown in the previous communication (1) that the slope index (S.I.) of vinyl polymers was found to be proportional to the product of three fundamental molecular parameters:

(i) the average cohesive energy per main-chain atom; U/N, which represents the enthalpic interchain interaction.

(ii) the reciprocal of the internal rotational degrees of freedoms per main chain atom, N/H which represents the entropic intrachain interaction

(iii) the average spatial molecular volume per main-chain atom V/N .

The slope-index model is described by:

$$\text{S.I.} = k \times (U/N) \times (N/H) \times (V/N) \quad \text{-------------------} \quad (1)$$

k has a value of 16 with the appropriate units to make S.I. dimensionless.

Table I shows the excellent agreements obtained between the experimentally-observed S.I. values versus those predicted by the model.

Table I

Comparision of Predicted and the Experimental S. I. for different Vinyl Polymers *

Polymer	Predicted S.I.	Expt. S. I.
Poly(styrene)	1.59	1.59
Poly(vinyl cyclohexane)	1.40	1.35
Poly(butyl acrylate)	0.96	0.99
Poly(vinyl acetate)	0.90	0.95
Poly(ethyl acrylate)	0.90	1.08
Poly(methyl acrylate)	0.81	0.84
Poly(vinyl chloride)	0.68	0.70
Amorphous Poly(propylene)	0.48	0.50
Poly(isobutylene)	0.52	0.62

* Abstracted from Table III of Reference (1).

Figure 1 shows the dynamic storage modulus G' master curves obtained from this work for poly (3,3-dimethyl-butyl acrylate), poly (isobutyl acrylate), poly (2-ethyl hexyl acrylate), poly (iso-octyl acrylates) and poly (iso-decyl acrylate).

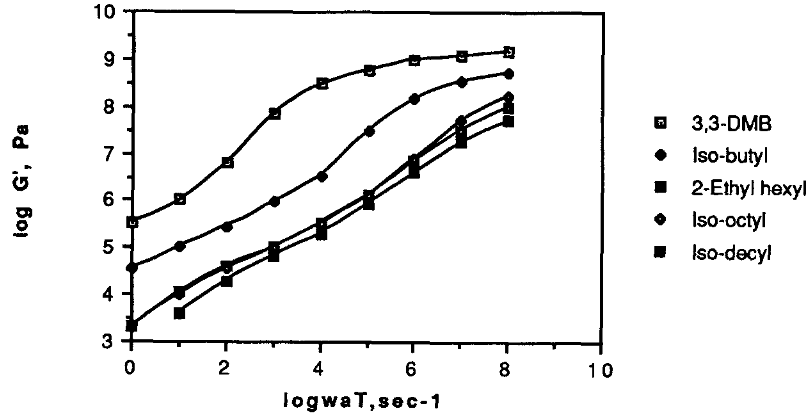


Figure 1: Dynamic storage modulus G' master curves for polyacrylates with different bulky side groups

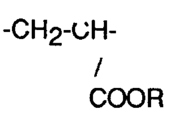
2)The modified slope-index models

One limitation of the original slope-index model is the poor prediction of the S.I. of vinyl polymers with bulky side groups (e.g. poly-2 ethyl-hexyl acrylate) or polymers with α– methyl group (e.g. poly-methyl methacrylate). The predicted values are much higher than those experimentally observed. The reason for such discrepancies can be attributed to the influence of the bulky side groups or α– methyl groups on the back-bone motion. It has long been recognized that the presence of bulky side groups or α–methyl group affect the glass transition temperature of the main-chain polymers (5). It is therefore understandable why the presence of such groups would also affect the relaxation behavior in the primary transition region, hence the slope index. In the modification of the model, we are assuming that the presence of such bulky side groups or α– methyl groups essentially increases the number of main-chain atoms on the backbone. In other words, the corrected number of main-chain atoms in such vinyl polymers is larger than the uncorrected number of 2 because of the presence of the bulky side groups or α -methyl groups.

Two different modifications of the slope-index model were made for
(1) Vinyl polymers with bulky side groups
(2) Polymers with α methyl group

3) Modified slope-index model for vinyl polymers with bulky side groups

In this case when the volume of the -CH(COO R)- (i.e. V_s) exceeds three times the volume of the main chain -CH_2CH- (i.e. V_m)



$$-CH_2-\underset{\underset{COOR}{/}}{CH}-$$

a corrected number of main chain atoms per repeating unit ; N_C, is needed: i.e.

$N_C = N + (V_s/V_m) - 3$ ---------------------------- (2)

Where N is the uncorrected number of main-chain atom =2, in vinyl polymers.

Table II shows examples how the number of main-chain atoms is being corrected, while Table III shows values of parameters affecting SI for the polymers.

Table II

Correction of number of main-chain atoms for polyacrylates with different bulky side groups.

-CH_2-CH -	Polymer	Vs	Vm	# Main Chain Atoms
/		x 10^5	x 10^5	Corrected/(Uncorrected)
COO(R)		(m3/mol)	(m3/mol)	
R= $(CH_2)_3CH_3$	Poly butyl-acrylate	12	4.44	2 / (2)
R= $CH_2CH(CH_3)_2$	Poly-isobutyl-acrylate	12	4.44	2 / (2)
R= $(CH_2)_2C(CH_3)_3$	Poly-3,3-Dimethylbutyl acrylate	16.4	4.44	2.7 / (2)
R= $CH_2CH(Et)(CH_2)_3CH_3$	Poly-2-ethylhexyl acrylate	20.9	4.44	3.7 / (2)
R= $(CH_2)_5CH(CH_3)_2$	Poly-isooctyl acrylate	20.9	4.44	3.7 / (2)
R= $(CH_2)_7CH(CH_3)_2$	Poly-isodecyl acrylate	25.4	4.44	4.7 / (2)

Table III:

Values of Parameters affecting the SI for Polyacrylates with bulky side chains.

Polymer	$(U/N_C) x10^{-4}$ (J/mol)	$(N_C/H) x10^2$	$(V/N_C)x10^5$ (m3/mol)
Poly butyl-acrylate	2.01	3.64	8.22
Poly-isobutyl-acrylate	2.46	4.00	8.22
Poly-3,3-Dimethylbutyl acrylate	2.62	3.28	7.73
Poly-2-ethylhexyl acrylate	1.78	3.97	6.84
Poly-isooctyl acrylate	1.78	4.25	6.84
Poly-isodecyl acrylate	1.57	4.79	6.33

Table IV shows the comparison of the experimental slope indices versus the predicted values before and after modification of the model for some of the polymers with bulky side -chains. It can be observed that the modified model greatly improves the predicted values, giving very good agreements between the predicted versus those experimentally observed.

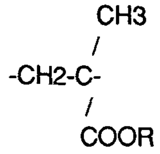
Table IV

Comparison of predicted versus experimental slope index for Polyacrylates with bulky side chains.

$-CH_2-CH-$ / COO(R)	Polymer	Predicted S.I. Corrected/Uncorrected	Expt. S.I.	Reference
R= $(CH_2)_3CH_3$	Poly butyl-acrylate	1.07 / (1.07)	0.99	1
R= $CH_2CH(CH_3)_2$	Poly-isobutyl-acrylate	1.24 / (1.29)	1.0	this work
R= $(CH_2)_2C(CH_3)_3$	Poly-3,3-Dimethylbutyl acrylate	1.06 / (1.43)	1.1	this work
R= $CH_2CH(Et)(CH_2)_3CH_3$	Poly-2-ethylhexyl acrylate	0.75 / (1.42)	0.70	this work
R= $(CH_2)_5CH(CH_3)_2$	Poly-isooctyl acrylate	0.88 / (1.62)	0.84	this work
R= $(CH_2)_7CH(CH_3)_2$	Poly-isodecyl acrylate	0.75 / (1.79)	0.71	this work

4) Modified slope-index model for vinyl polymers with α–methyl group

For polymers with α–methyl group (e.g. poly-methacrylates, poly-isobutylene, poly-α methyl styrene),



$$-CH_2-\overset{\overset{CH_3}{/}}{\underset{\underset{COOR}{/}}{C}}-$$

when V_s, i.e. volume of CH_3 -C(COOR)- exceeds V_m; the volume of the main chain -CH2-C- . Then the corrected number of main-chain atom

$N_c = N + (V_s/V_m) - 1$ ------------ (4)

Table V compares the corresponding predicted versus experimentally-observed S.I. values for polymers with α–methyl groups.

Table V

Comparison of Experimental verus Predicted Slope-Index Values for Vinyl Polymers with α-methyl group

$-CH_2-C(CH_3)-$ / R	Polymer	Predicted S.I. Corrected/(Uncorrected)	Expt. S.I.	Reference
R= CH_3	Poly -isobutylene	0.52	0.62	8
R= C_6H_5	Poly-α–methyl styrene	1.24 / (2.14)	1.0	this work
R= $COOCH_3$	Poly-methyl methacrylate	1.05 / (1.42)	0.84	this work
R= $COOCH_2CH_3$	Poly-ethyl methacrylate	0.92/ 1.47	0.66	9,14
R= $COO(CH_2)_3CH_3$	Poly-butyl methacrylate	0.77 / 1.61	0.68	10,14
R= $COO(CH_2)_5CH_3$	Poly-hexyl methacrylate	0.68 / 1.77	0.84	11,14
R= $COO(CH_2)_7CH_3$	Poly-octyl methacrylate	0.62 / 1.94	0.74	12,14
R= $COO(CH_2)_{11}CH_3$	Poly-dodecyl methacrylate	0.57 / 2.29	0.72	13,14

Conclusion

Modified models for the prediction of the slope index of the viscoelastic master curve in the primary transition region for vinyl polymers with either bulky side groups or α-methyl groups have been proposed. Very good agreeements between predicted and experimental values are found. The modified models take into account of the effect of the bulky side group or α-methyl groups in the contribution to the corrected number of the main-chain atoms. The predicted slope index was found to be proportional to (i) the average cohesive energy per main-chain atom; U/N, which represents the enthalpic interchain interaction, (ii) the entropic intrachain interaction as defined by H/N, and (iii) the average spatial molecular volume per main-chain atom V/N .

Acknowledgement

The author would like to thank Mr. Randy Chapman, Ms. Debbie Chiu, Ms. Eileen Shearin and Mr. R. V. Ham for their technical assistance, Drs. K.S.C. Lin, N. F. Phelan, K. Josephy, D. H. Kaelble and Professor J. J. Aklonis for valuable discussions aand suggestions, and Avery for permission to publish this work.

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Accepted June 26, 1990 K