Estimating Cross-sectional Area of a Polymer Chain by Additive Method

The cross-sectional area of a polymer chain, which, as a structural parameter, has been correlated to a number of properties,[1-3] can generally be calculated with the following equation:
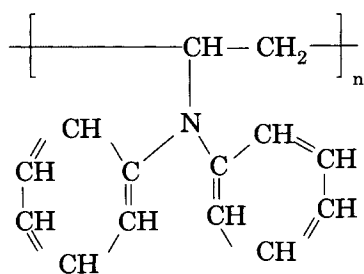
$$A = V/n_1 \cdot c \tag{1}$$

where V is the volume of a crystal cell, n_1 the number of polymer chains per crystal cell, and c the periodic distance. The relationship between glass transition temperature, cohesion energy density, and chain cross-sectional area of a polymer has been established.[3] It is well known that glass transition temperature, as well as cohesion energy density of a polymer can be estimated by adding the values of group contributions to glass transition temperature from the structure of repeating units of a polymer.[4] Therefore, if the values of group contributions to chain cross-sectional area are known, it is possible to evaluate the area in terms of the structure of a polymer chain and, furthermore, to reveal the structure–property relationship of a polymer. This paper presents our attempt to find the contribution of an individual chemical group to cross-sectional area of a polymer chain and our proposed correction which should be made for the additive method used for estimating chain cross-sectional are.

Based on the additive method, a chain cross-sectional area can be obtained by adding all the group contributions of a repeating unit of a polymer chain:
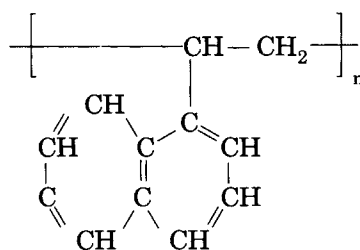
$$A = \sum_i n_i \cdot a_i \tag{2}$$

where n_i is the number of group i in a repeating unit and a_i the value of group i contributions to chain cross-sectional area. These group contribution values of Table I are obtained in this work.

For most vinyl polymers and polydienes the chain cross-sectional area obtained with Eq. (2) is agreement with that from Eq. (1) (Table II). It is noticed, from Table II, that for poly-o-methylstyrene and poly-m-methylstyrene the contribution value of methyl group in Table I should be doubled because methyl group is attached to the m-position of a phenyl ring. In the case of carbazole group of poly-N-vinylcarbazole and naphthalene group of poly-1-vinylnaphthalene (Table II), their contribution values are twice that of the phenyl ring.

Poly-N-vinylcarbazole   Poly-1-vinylnaphthalene

The presupposition for using additive method is that the group contributions are independent of each other. If interaction between the groups is considered, some correction for Eq. (2) must be made, as proposed below:

TABLE I
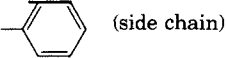Values of Group Contribution to Cross-sectional Area of a Polymer Chain

Group	$a_i(nm^2)$	Group	$a_i(nm^2)$
$— CH_3$	0.16	$>CH_2$	0.10
$\equiv CH$	0.08	$— C —$	0.00
$— CH_2CH_3$ (side chain)	0.34	$— CH(CH_3)_2$ (side chain)	0.49
$— CH(CH_3)_3$ (side chain)	0.66	$>C=O$	0.5
$— CH = CH —$	−0.13	$\equiv CCH_3 —$	0.05
$— CH = CH_2$ (side chain)	0.25	$— O —$	0.07
$— CN —$	0.12	$— N<$	0.10
$— H$	0.00	$— OH$ (alcohol)	0.03
$— OH$ (acid)	0.12	(phenyl) (side chain)	0.50
Cyclopropyl	0.35	Cyclobutyl	0.55
Cyclopentyl	0.78	Cyclohexyl	0.98
Cycloheptyl	1.18	F (single)	0.03
F (twinned as in CF_2)	0.07	Cl (single)	0.09
Cl (twinned)	0.12	Br (single)	0.12
Br (twinned)	0.16		

TABLE II
Chain Cross-sectional Area of Vinyl Polymers and Polydienes (nm²)

Polymer	From Eq. (1)[a]	From Eq. (2)
1,2-Polybutadiene	0.432	0.43
1,4-Poly-2,3-dimethylbutadiene	0.297	0.30
1,4-Poly-1,3-pentadiene	0.239	0.23
Poly-3-cyclohexylpropene	1.219	1.26
Polyvinylcyclohexane	1.209	1.16
Poly-N,N-dibutylacrylamide	1.498	1.51
Poly-1-methylpropyl vinyl ether	0.833	0.85
Polymethyl methacrylate	0.641	0.61
Polychlorotrifluoroethylene	0.356	0.33
Polytrifluoroethylene	0.271	0.25
Poly-o-methylstyrene	0.903	0.86
Poly-m-methylstyrene	0.981	1.00
Poly-N-vinylcarbazole	1.310	1.28
Poly-1-vinylnaphthalene	1.123	1.20

[a] Using the parameter of crystal cell of polymers cited in Ref. 5.

TABLE III
Chain Cross-sectional Area of Polyolefine

Polymer	From Eq. (1)	From Eq. (2)	From Eqs. (3)-(4)
Polypropylene	0.344	0.34	—
Polybutene-1	0.452	0.44	—
Polyiso-butene	0.415	0.42	—
Polypentene-1	0.583	0.54	0.61
Polyhexene-1	0.787	0.64	0.77
Poly-4,4-dimethylpentene-1	1.030	0.76	0.97
Polytetradecene-1	2.100	1.44	2.08
Polyhexadecene-1	2.370	1.64	2.41
Polyoctadecene-1	2.640	1.84	2.74

$$A = \sum_i n_i \cdot a_i + \Delta A \tag{3}$$

For many polyolefines with side groups each containing more than three carbon atoms, its chain cross-sectional area calculated from Eq. (2) does not coincide with that from Eq. (1), as the bulky side groups play an role in the interaction between the polyolefine chains. Therefore, it is necessary to use Eq. (3) to estimate chain cross-sectional area of such polyolefines. In such cases, the corrected term, ΔA, of Eq. (3) for polyolefine is

$$\Delta A = -0.164 + 0.638 \sum_i n_i^s \cdot a_i^s \tag{4}$$

where the superscript s refers to side group. The chain cross-sectional area values of some polyolefines calculated by Eqs. (3) and (4) are listed in Table III.

The chain cross-sectional area values of polyoxide $+(CH_2)_n-O+_p$, polyester $+CO-(CH_2)_n-COO-(CH_2)_m-O+_p$, and polyalkenemer $+CH=CH-(CH_2)_n+_p$ do not change with the number of -CH_2- groups of the repeating units (Table IV). This may be attributed to the zig-zag conformation of their chains.[2] For these polymers the correction terms in Eq. (3) are as follows: for polyoxide

$$\Delta A = 0.104 - 0.1 \cdot N \tag{5}$$

for polyester

$$\Delta A = -0.255 - 0.1 \cdot N \tag{6}$$

TABLE IV
Chain Cross-sectional Area of Polyoxide, Polyester and Polyalkenamer

Polymer	From Eq. (1)	From Eq. (2)	From Eqs. (5)-(7)
Polyoxymethylene	0.173	0.17	0.174
Polyhexamethylene oxide	0.182	0.67	0.174
Polydodecamethylene oxide	0.183	1.27	0.174
Polyethylene oxalate	0.200	0.64	0.184
Polyethylene adipate	0.182	1.04	0.185
Polyhexamethylene sebacate	0.185	1.84	0.185
Polycyclopentene	0.181	0.17	0.185
Polycyclooctene	0.185	0.47	0.185
Polycyclododecene	0.185	0.87	0.185

for polyalkenamer

$$\Delta A = 0.315 - 0.1 \cdot N \tag{7}$$

where N is the number of $-CH_2-$ groups in a repeating unit of a polymer chain. In Table IV, chain cross-sectional area values corrected by Eqs. (5)-(7) are listed.

The chain cross-sectional area values of 90 polymers added over all the group contributions of a repeating unit of a polymer chain by using Eqs. (2)-(7) are in good agreement with those obtained with Eq. (1). The error of mean square is 5% and the error of 80% studied polymers are less than this error of mean square, which, we think, is satisfactory.

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