Molecular Simulations of the Conformational Properties of Atactic Poly(2-ethylbutyl methacrylate)

Rahul B. Karyappa, Upendra Natarajan*

Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411 008, India

ABSTRACT: RIS Metropolis Monte Carlo (RMMC) simulations were used to determine the unperturbed theta-state chain dimensions of atactic stereoconfigurations of poly (2-ethylbutyl methacrylate) [PEBMA]. Root mean-squared end-to-end distance $(\langle r^2 \rangle_o / M)^{1/2}$ and characteristic ratio (C_n) were calculated along with the backbone torsion angle distribution. The simulated properties are in very good agreement with experimental results. The values of the PEBMA chain dimensions are in-between those corresponding ones for poly(*n*-butyl methacrylate) and poly (*n*-hexyl methacrylate) thereby showing the effect of branching in the side-chain. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1586–1591, 2012

Key words: Monte Carlo simulation; poly(2-ethylbutyl methacrylate); vinyl polymer; chain dimensions; conformations

INTRODUCTION

Configurational properties of polymer chains serve as an important first step towards the calculation and understanding of physical properties of fundamental and practical interest involving thermodynamic, kinetic, and viscoelastic behavior, be it in solution or in the bulk state. The conformations of polymer chains determine quantitatively and are also widely accepted to be responsible for the behavior of polymeric materials in the condensed bulk phase. Properties such as rubber elasticity, the hydrodynamics and thermodynamics of polymer solutions, and optical properties are few examples of several properties that are dependent on chain conformations. The conformationally averaged dimensions under theta condition and in the melt state are well-known to be very similar, and therefore, a calculation of these properties under theta condition would even serve to predict or correlate with melt-state properties wherein, for example, the ductility of amorphous polymers are known to scale with entanglement properties which in turn are known to scale with chain dimensions. Therefore, a prediction of chain dimensions can lead to reasonable estimates of viscosity, stiffness, mechanical toughness of amorphous polymers, and the rheological properties of polymers.

Present address: Upendra Natarajan, Visiting Associate Professor, Department of Chemical Engineering, Indian Institute of Technology (I.I.T.) Madras, Chennai 600036, India.

Correspondence to: U. Natarajan (unatarajan@iitm.ac.in).

The best method in the most convenient manner to calculate the statistical properties of polymer chains in the melt or in theta solvents is the Rotational Isomeric State theory,[1] which requires the derivation of statistical weights before it can be implemented. This theory has been extensively applied to many polymers over several decades.[2] The RIS method would be a preferred one for calculations on linear homopolymers and copolymers, when statistical weight matrices are available and known accurately. Derivation of these statistical weights is a relatively tedious process even for a simplest of chain structures. It is also not possible to treat branched chains including graft polymers and copolymers in a convenient manner in the RIS approach.

An alternative method, RIS Metropolis Monte Carlo (RMMC) was developed by Honeycutt,[3] which provides a direct estimation of several conformational properties of the polymer chains, using fully atomistic simulations via force-field based potential energy calculations in continuum space, thereby avoiding the drawbacks of the traditional RIS theory. At the theta state the long-range interactions along the chain effectively vanish. Therefore, to mimic this condition, a bond-based cutoff parameter for nonbonded interactions is employed (namely *max_bonds*) in the RMMC simulation. Of course, the minimum number of bonds separating two atoms that need to be considered to taken into account nonbonded interactions (within the same chain) would be 3. In the RMMC simulation, an optimization of the simulation parameters is very important, as RMMC simulations are significantly more expensive than the RIS method in terms of calculation time.

The RMMC method has been implemented for the simulation of polymers with a variety of structural repeating units.[4–12] These simulations have looked at the characteristic ratios C_n and persistence lengths (L_p) of liquid crystalline polyesters (LCPEs)[4] containing the dihydroxy-α-methylstilbene (DHαMS) fragment, and on VECTRA[TM] A900 (a commercial LCPE). It was observed that the DHαMS containing polycarbonate chain was much stiffer than an ordinary random coil polymer, but much more flexible than any of the LCPEs modeled. J. For random terpolymers[5] of DHαMS terephthalate, DHαMS isophthalate and DHαMS 2,6-naphtholate (mole fractions 0.65, 0.10, and 0.25, respectively) were studied by RMMC simulations and experiments to investigate the effects of weight-average molecular weight (M_w) on the radius of gyration (R_g) and intrinsic viscosity [η]. The single chain properties, mean-squared end-to-end distances, radii of gyration, characteristic ratios, and persistence lengths have been calculated for polyester chains with isolated carboxyl groups,[6] for poly(methyl acrylate), poly(methyl methacrylate), and poly(vinyl acetate) and some aliphatic main chain polyesters having alkyl chains of various lengths between the carboxyl groups. The effects of the run parameters (i.e., cut-off for nonbonded interactions and chain length) on the results were discussed.

Conformational properties of polyesters based on terephthalate and cyclohexylene dicarboxylate with 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol have been investigated[7] on chains having two different configurations, one with an all *trans* linkage of 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and the other in which both *trans* and *cis* linkages of these rings in the diol units were present. Incorporation of *cis* isomers results in a decrease in the chain dimensions, and reduces the influence of the repeat unit chemical structure on the overall averaged chain dimensions. The effect of temperature, isomer linkage, nature of the aliphatic ring in the backbone and its content, on the overall chain dimensions, and the persistence lengths, was obtained by that study. The single chain conformational properties of bisphenol-A-polycarbonate[8] under various solvent conditions (including theta state), and the properties (characteristic ratio and persistence length) for poly(L-lactic), poly(L,D-lactic), and poly glycolic acids (PLLA, PLLA/PDLA, and PGA, respectively)[9] have predicted the PLLA/PDLA chains to be most flexible, with the characteristic ratio being 6.5 for the copolymer with alternating L,D-dyads, and 6.8 for the copolymer with random combination of L,D- and D,L-dyads; whereas, PLLA chains were found to be the least flexible (with a characteristic ratio 7.7). The dependence of the characteristic ratios on the cut-off limit was also found to be different in the calcula-

tions with the modified and original polymer consistent force field (PCFF). More recent studies have looked at liquid-crystalline polyesters,[10] and aromatic copoly(ester-amide)s,[11] poly(methacrylate)s containing side-groups and side-chains under theta condition.[12]

Dilute solution properties (chain dimensions and intrinsic viscosity) of poly(methacrylates) have been investigated experimentally.[13–18] These reports have looked at the dilute solution properties of a series of *n*-alkyl methacrylate homopolymers, such as the methyl, ethyl, butyl, hexyl, 2-ethylbutyl, octyl, and lauryl structures, wherein the relationship between intrinsic viscosity, mean-squared end-to-end distance, and molecular weight has been obtained by the use of light-scattering and viscosity measurement techniques in good solvents as well as in various ideal (theta) solvents. The effect of the size of the pendant (side) groups on the degree of chain extension of the series of alkyl methacrylate polymers in ideal solvents was discussed. A critical review containing reliable data on chain flexibility of polymethacrylates is available,[19] with an attempt to elucidate the trends regarding the effect of the nature of the side-group on chain flexibility. Based on experimental studies, the relationship between polymer conformational characteristics, i.e., unperturbed chain dimensions and their variation with temperature and polymer structure have been reviewed and critically discussed,[20] wherein emphasis was placed on structure/conformation relationships for structurally well-defined polymethacrylates, polydienes, and polyolefins.

The present study in this article provides the results of RMMC simulations conducted on atactic poly(2-ethylbutyl methacrylate) (PEBMA) at the theta-condition. In the case of poly(2-ethylbutyl methacrylate), the pendant group length is that of butyl while the molecular weight is that of the hexyl group. The chemical structure of the repeat unit is shown in Figure 1. Simulations were done at two different molecular weights (chain lengths). The unperturbed chain dimensions, i.e., root-mean square end-to-end distance by molecular weight $(\langle r^2 \rangle_o / M)^{1/2}$, root-mean-squared radius of gyration $(\langle s^2 \rangle_o / M)^{1/2}$, and the characteristic ratio C_n were calculated by RMMC simulations and compared with experimental results available in the literature[18,19] for this polymer with *meso* dyad fraction and tacticity distribution typical of PEBMA as synthesized under bulk solution condition using free-radical addition polymerization.

THEORETICAL SECTION

We present here a brief description of various geometric conformational properties of chains that are
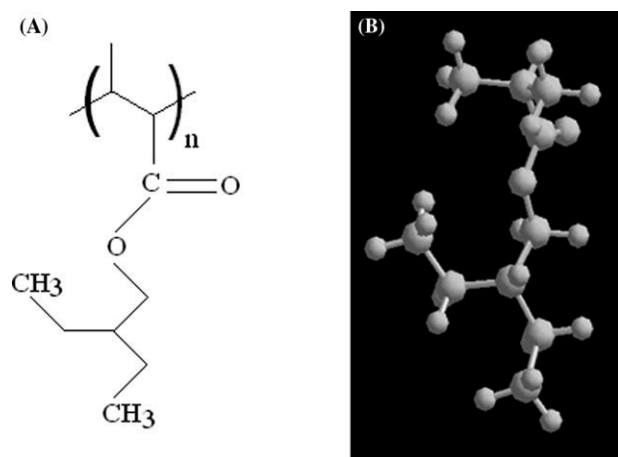
Figure 1 A: Repeat unit structure of poly(2-ethylbutyl methacrylate) (B) Ball and stick model.

directly relevant in the context of the present study. The squared end-to-end distance r^2 of a chain is a scalar property obtained by taking the dot product of the end-to-end vector with itself; with its value being dependent on the specific overall conformation adopted by the polymer chain, which in turn is highly dependent on the conformational states adopted at each rotatable bond in the polymer chain backbone.[1] This is essentially the square of the magnitude of the end-to-end vector of the chain. When the squared end-to-end distance is averaged over all possible conformations, we define therefore the mean-squared end-to-end distance $\langle r^2 \rangle$ that is a property equivalent to that obtained by averaging over a reasonable extent of time given the dynamics of the chain in a solvent (i.e., in solution). Therefore, the conformationally averaged squared end-to-end distance is a property that can be measured experimentally.

Another quantity of interest is the squared radius-of-gyration, s^2, which is the square of the sum of the deviations (displacements in x, y, z coordinates) of each atom in the polymer backbone from the mean position of the entire chain. This quantity, essentially a 1st order tensor (i.e., a vector) is reflective of the shape of a polymer chain. When averaged over all possible conformations which a polymer chain can adopt in solution, we obtain and define the mean-squared radius-of-gyration $\langle s^2 \rangle$ which can be experimentally measured using static light scattering technique. The radius of gyration is also related to the physical properties such as the entanglement density of a chain in the melt state or the amorphous glassy state. The radius of gyration of a chain in solution is very useful in direct determination of the intrinsic viscosity of a dilute polymer solution.

The characteristic ratio,[1] C_n $(= \langle r^2 \rangle / nl^2)$ defined as the ratio of $\langle r^2 \rangle$ to the corresponding value of a freely-jointed chain (given by nl^2 with l being the mean bond length of a repeat unit in a n-repeat unit chain) provides a measure of the flexibility (and stiffness) of a polymer chain. A relatively higher value of C_n refers to conformationally stiffer chains such as the rigid rod type, while lower values (typically in the range 2–12) refer to either flexible or some semiflexible chains. C_n attains a constant limit for high molecular weights and under those conditions it is termed as C_∞. The characteristic ratio is a very useful physical property of a polymer chain and is useful in the determination of entanglement density as well as ductility of an amorphous polymer. This is also related to and gives a measure of the mechanical modulus of a polymeric material.

The persistence length,[1] which is another measure of chain stiffness, is a scalar quantity, and is calculated as the sum of the projection of all bonds in a polymer chain on to the first bond, averaged over all possible conformations of the chain. Higher values of persistence length refer to stiffer chains, given that the effect of the orientation of a particular bond in the chain persists longer along the bonds in the backbone, and therefore in a sense less number of conformational states can be adopted by the chain to realize a randomization of the spatial orientations of the bonds. The origin of all these important properties of a polymer chain lies in the conformational states and the distribution of the probability of the states at each torsion angle in the chain backbone.

COMPUTATIONAL DETAILS

The monomer unit corresponding to PEBMA is shown in Figure 1. Cerius2 molecular modeling package[21] was used to set up the chains and for running the RMMC simulations on Silicon Graphics Octane workstation. The advanced PCFF[22] was used for the generation of chains. Dielectric constant $\varepsilon = 1$ was used for calculation of the electrostatic energy. For all simulations in the present study, we have used a maximum bond cut-off value (max_bond) of 6 for the nonbonded interactions between atoms in the same polymer chain. Typically, a value in the range 6–8 has been utilized in the literature[3,4,7–10,12] for simulations of relatively stiffer polymers such as polyesters and LCPs and polymers with acrylic and ester groups including those with side-chains. If two atoms in the chain are separated by more than this number of bonds, then their possible interactions were neglected. The minimum bond cutoff (min_bond) used in the simulations here reflects the minimum value of the number of bonds separating any two atoms along the chain to treat their mutual interactions. This value was taken as 3 as per the "pentane effect." A max_bond value of 4 is applicable to polyolefins.[3]

TABLE I
Simulated Chain Dimensions and Experimental Values of Atactic Poly(2-ethylbutyl methacrylate) (PEBMA) at theta
(θ) Condition at Room Temperature (300 K)

Mol. wt.	$(\langle r^2 \rangle_o/M)^{1/2}$ Å (g/mol)$^{-1/2}$		$(\langle s^2 \rangle_o/M)^{1/2}$ Å (g/mol)$^{-1/2}$		C_∞	
	Expt.[a]	Simu	Expt.	Simu.	Expt.[b]	Simu.
34,053	0.51	0.54 ± 0.19	–	0.22 ± 0.01	9.8	9.67 ± 1.30
59,591		0.54 ± 0.19	–	0.22 ± 0.01		9.74 ± 1.17

Meso dyad fraction is 0.25 based on the experimental value for chains synthesized using free-radical polymerization in bulk solution.
[a] J Polym Sci 1960, 43, 557.
[b] J Macromol Sci Rev Macromol Chem Phys C 1988, 28, 371.

The calculations were made on sets of chains having two different chain-lengths (200 and 350 repeat units corresponding to molecular weights 34,053 and 59,591). For each of these molecular weights, 50 conformationally independent chains were generated by a Monte Carlo simulation with *meso* dyad fraction 0.25, as per experimental data available,[18,19] in each chain using Bernoullian statistics in the simulation here reflecting the actual distribution of tacticity in these polymethacrylates as per actual experimental conditions of free-radical polymerization in bulk solution. The simulation procedure described here was performed on the two sets of chains pertaining to lower (34,053) and higher (59,591) molecular weights. Each chain was energy-minimized by steepest descent and conjugate gradient methods to energy-gradient convergence 0.01 kcal/mol. Following this stage, molecular dynamics simulation (NVT) of 10 ps was performed on the selected five low energy chains at 300 K. After 10 ps MD simulation, these five chains were energy-minimized using the conjugate-gradient method. Finally, three chains were chosen on the basis of the lowest potential energy and independent RMMC simulations were performed on these chains. In the RMMC 600,000 steps were used for the equilibration section and 1,500,000 steps were used for the production section for calculating the averaged properties. Such long runs are typical of RMMC on these types of polar polymers from our earlier work.[7,12] The "snapshots" for updating the chain conformational properties were taken at 2000 steps interval. The RMMC simulations were performed at 300 K.

RESULTS AND DISCUSSION

Table I shows the RMMC simulation results observed for the atactic PEBMA with the *meso* dyad fraction 0.25. The values of the mean-square end-to-end distance, mean-squared radius of gyration, and characteristic ratio obtained for two different chain lengths are in very good agreement with the experimental results available in literature.[18,19] The simulated chains based on the extensive RMMC runs,

showed the well-known Gaussian behavior for which the ratio $\langle r^2 \rangle_o/\langle s^2 \rangle_o$ should be exactly 6, particularly a characteristic of flexible chains. Therefore, atactic PEBMA is not a stiff polymer, even though it has a long side-chain with polar groups that can interact and hinder rotation of backbone bonds, and this is also reflected by the value of its characteristic ratio, simulated here as well as available from experiments in literature.[19] The possible reasons for its backbone flexibility could be the small size of the chemical groups present in the side-chain, and, its atactic stereochemical nature. It is well known[1,2] that for vinyl polymers, including polymethacrylates, the isotactic as well as syndiotactic versions of the chains are rather rigid and could adopt either a near all-*trans* or helical conformations. The characteristic ratio value can depend in general on several factors: (1) the volume occupied by the side group, (2) the distance of the center-of-mass of the side-group from the backbone of the chain, (3) the flexibility of the side group, and (4) the chemical nature of the side group (which may lead to polar or other interactions).

Figure 2 shows two snapshots of the PEBMA chain taken from the equilibrated section of the Monte Carlo simulations that were performed on two independently generated (conformationally sufficiently different) initial chains, for molecular weight 34,053, having fairly similar chain dimensions close to their conformationally averaged values under theta condition. This shows the complexity of the configuration adopted by the polymer and the complexity involved in the computational simulation of these high molecular weight polymethacrylate chains.

Figure 3 shows the backbone dihedral distribution for PEBMA obtained from the RMMC simulations. PEMBA, where there is branching on the pendant group, the length being that of butyl group, while the molecular weight being that of the hexyl group, shows greater chain extension as compared to poly(*n*-butyl methacrylate) PnBMA chain[12,15,19] (expt. value $C_n = 8.9$ for *meso* dyad fraction 0.21 from Ref. 19), but considerably lesser extension than poly(*n*-hexyl methacrylate) PnHMA chain[12,16,19]
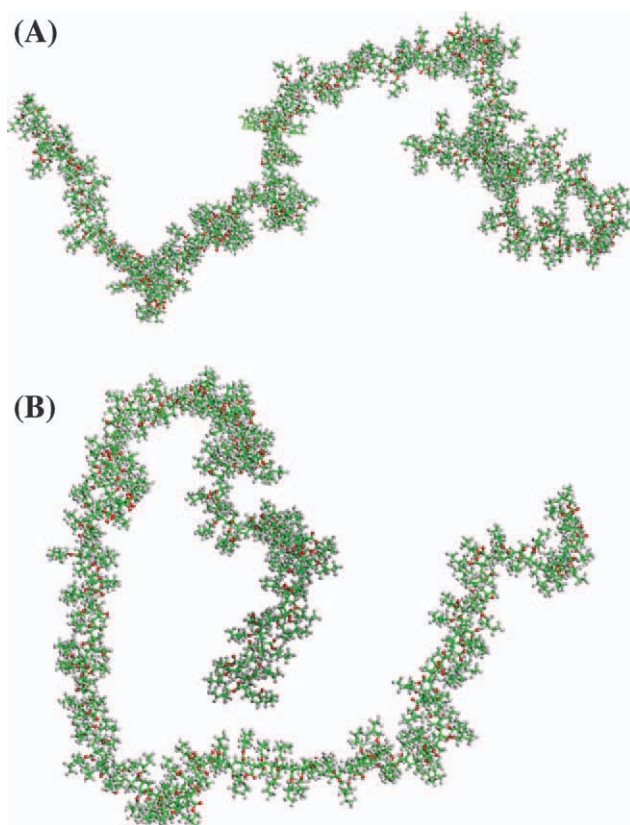
Figure 2 Two different PEBMA relaxed chain (200 repeat unit) configurations obtained as a snapshot from the equilibrated section of the RMMC simulations. The *meso* dyad fraction is 0.25 based on experimental value for real chains. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(expt. value $C_n = 11.2$ for *meso* dyad fraction 0.21 from Ref. [19]). This effect seems to manifest itself in the relative proportions of the *trans* versus *gauche* conformers along the backbone bonds which directly control the chain dimensions under theta conditions, with the interesting influence primarily originating from the branched nature of the 2-ethylbutyl side-group in comparison with the unbranched *n*-butyl and *n*-hexyl side-groups. This behavior is found to go in accordance with the relative proportion of *trans* (near *trans* or extended) conformational states to the gauche (kinked) conformational states of the chains in these polymers, as obtained from the data on PEBMA in the present work in comparison with those observed for PnBMA and PnHMA chains from earlier work in the literature.

A comparison of the torsion distribution shown in Figure 3 here for PEBMA with the distributions for the corresponding backbone bond for linear polyethylene (PE) and polyethylene-like molecule *n*-decane,[3] shows that for the torsion angle in the case of PEBMA the difference between the probabilities of the preferred *trans* state and the less-preferred *gauche* states is greater in value than that which is seen for

this torsion angle in linear polyethylene[3] as well as *n*-decane,[3] and this behavior can be rationalized to be due to the presence of the side-chain in PEBMA which renders stiffness to the polymer chain in comparison to polyethylene. This behavior is also reflected directly in the conformationally averaged mean-squared end-to-end distance as well as characteristic ratio (PEBMA has much higher values as compared to PE). The torsion distribution seen for backbone bonds in polyesters such as PET as well as those in polyesters constituted by cycloaliphatic chemical groups in the backbone[7] show an even higher relative probability for the extended trans conformational state at some (not all) of the rotatable backbone bonds. Polyesters[7] and LCPs[4,5,10] as known from RMMC simulations are comparatively stiffer as compared to PEBMA. The "relative energies" (i.e., energy difference with respect to the global minima) for the energy minima conformational states for rotation about the C—C bonds for chemically simple polymers such as linear polyethylene and atactic-polypropylene, in comparison to the barrier for rotation in PEBMA here, are smaller. Low values of "relative energies" mean high probability of occurrence as manifested in the torsion distribution diagram. A comparison of the probability distribution for this torsion in PEBMA with those in other polymethacrylates containing side-groups and side-chains[12] clearly indicates the higher probability of a *trans* (extended) state relative to the *gauche* (kinked) state for some polymethacrylates such a poly(phenyl methacrylate) and poly(*n*-hexyl methacrylate). Even though the backbone bonds are constituted by very different atoms in the PEBMA repeat unit as compared to those in bisphenol-A polycarbonate repeat unit[8] for
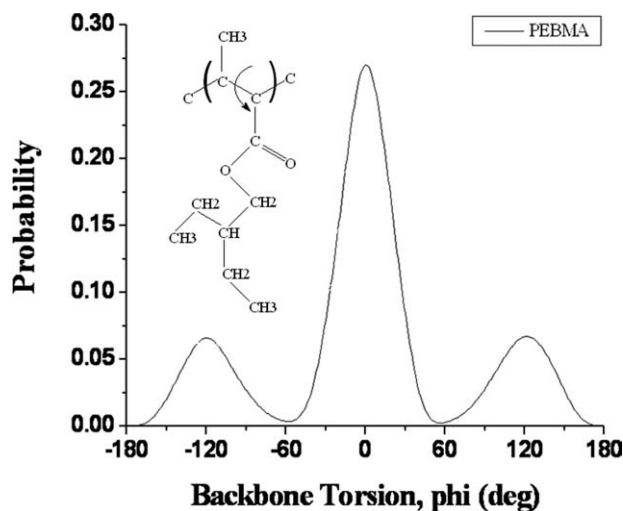

Figure 3 Backbone torsion distribution of a 200 repeat unit poly(2-ethylbutyl methacrylate) chain for *meso* dyad fraction 0.25 based on experimental data (see Table I). Inset show repeat unit with the backbone carbon atoms participating in the torsion specified.

facilitating a direct comparison of the torsions, the BPAPC repeat unit is much more conformationally stiffer ($\langle \mathbf{r}^2 \rangle_{\mathbf{o}}/M = 1.01$ for BPAPC as compared 0.54 for PEBMA) given the presence of the phenylene rings and the carbonate group.

CONCLUSIONS

RMMC enables the direct estimation of several key conformational properties of polymer chains by atomistic simulations using an all-atom force-field. Single chain properties of atactic PEBMA representative of the theta solution condition have been calculated using RMMC simulations in this work. The calculated chain dimensions of the PEBMA, mean-squared end-to-end distance, and characteristic ratio are in good agreement with the chain properties studied experimentally on this polymer. The averaged chain dimensions of PEBMA is greater than that of poly(n-butyl methacrylate) but less than that of poly(n-hexyl methacrylate), thus bringing out the effect of branching in the side-chain within the alkyl poly(methacrylates) class of polymers. The simulations show that the atactic-PEBMA chains behave in a Gaussian manner, exemplifying flexible or semi-flexible nature rather than stiff nature, even though containing a relatively long pendant side-chain. PEBMA chains are found to be conformationally stiffer relative to linear polyethylene, but relatively flexible in comparison with bisphenol-A polycarbonate, polyesters, cycloaliphatic polyesters, and LCPs that are known in literature.

References

1. Flory, P. J. Statistical Mechanics of Chain Molecules; Wiley Interscience: New York, 1969.
2. Rehahn, M.; Mattice, W. L.; Suter, U. W.; Adv Polym Sci 1997, 131/132, 1.
3. Honeycutt, J. D. Comput Theor Polym Sci 1998, 8, 1.
4. Bicerano, J. Comput Theor Polym Sci 1998, 8, 9.
5. Bicerano, J.; Brewbaker, J. L.; Chamberlin, T. A. Comput Theor Polym Sci 1998, 8, 15.
6. Blomqvist, J.; Pietilä, L.-O.; Mannfors, B. Polymer 2001, 42, 109.
7. Sulatha, M. S.; Purushotam, S.; Natarajan, U. Polymer 2002, 43, 6295.
8. Lee, S.; Ho, Y. J.; Lee, H. Comput Theor Polym Sci 2001, 11, 219.
9. Blomqvist, J. Polymer 2001, 42, 3515.
10. Pavel, D.; Yarovsky, I.; Shanks, R. Polymer 2005, 46, 2003.
11. Teoh, M. M.; Chung T. S.; Schiraldi, D. A.; Cheng, S. X. Polymer 2005, 46, 3914.
12. Karyappa, R. B.; Natarajan U. J Macromol Sci B 2008, 47, 1075.
13. Chinai, S. N.; Matlack, J. D.; Resnick, A. L.; Samuels, R. J. J Polym Sci 1955, 17, 391.
14. Chinai, S. N.; Samuels, R. J. J Polym Sci 1956, 19, 463.
15. Chinai, S. N.; Guzzi, R. A. J Polym Sci 1956, 21, 417.
16. Chinal, S. N. J Polym Sci 1957, 25, 413.
17. Chinai, S. N.; Resnick, A. L.; Lee, H. T. J Polym Sci 1958, 33, 471.
18. Chinai, S. N.; Didot, F. E.; Levi, D. W. J Polym Sci 1960, 43, 557.
19. Mays, J. W.; Hadjichristidis, N. J Macromol Sci C Rev Macromol Chem Phys 1988, 28, 371.
20. Xu, Z.; Hadjichristidis, N.; Fetters, L. J.; Mays, J. W. Adv Poly Sci 1995, 120, 2.
21. Cerius2. Polymer User Guide; MSI: San Diego, 1998.
22. Maple, J. R.; Hwang, M.-J; Stockfisch, T. P.; Dinur, U.; Waldman, M.; Ewig, C. S.; Hagler, A. T. J Comput Chem 1994, 15, 162.