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REGULAR ARTICLE

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Properties of modified cyclo-olefin copolymers predicted by ab initio and molecular simulation techniques

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Abstract Mechanical, thermal and optical properties of modified cyclo-olefin copolymers COC were studied by molecular dynamics simulations and ab initio calculations. The COC chains were modified by substituting the norbornane rings with methyl groups and replacing ethane units with propane. A modified Dreiding 2.21 force field was developed for the molecular dynamics simulations. The bulk and Young's moduli increased when the norbornane rings of COC were substituted with methyl groups and when the ethane units were replaced with propane. The highest glass transition temperature was obtained when the norbornane rings were substituted with methyl groups. Ab initio calculations of isotropic polarizability and refractive index were sensitive to the applied basis set and level of theory. Good agreement with available experimental data was obtained with the B3LYP/6-311G** method. Replacement of ethane units with propane lowered the refractive index significantly, whereas other structural modifications had practically no effect.

Keywords Modified cyclo-olefin copolymers · Force field · Ab initio · Physical properties · Refractive index

1 Introduction

Cyclo-olefin copolymers (COC) are amorphous or semicrystalline thermoplastics, which are manufactured by copolymerization of cyclo-olefin and olefin monomers. Typically, cyclic monomer is norbornene or a derivative of norbornene, and the olefin is ethylene or propylene. [1–6] COC have several useful properties, such as optical clarity, excellent dielectric strength, moisture barrier, high temperature resistance and good mechanical properties [6].

The manufacture and properties of COC have been studied extensively by experimental techniques, with a focus on the improvement of manufacturing technologies [7–16]. Theoretical studies have mostly been carried out on polynorbornane polymers and on COC prepared from ethylene and norbornene. [17–27] COC based on propylene or derivatives of norbornene have been studied to some extent [1, 2, 28–35]. An ability to predict the effects of structural modifications would assist in the attempt to prepare mechanically stronger COC materials with good optical and thermal properties.

Although, second-generation polymeric force fields, such as PCFF [36–43] and COMPASS [44], have frequently been applied in studies on polymer properties, they are unsuitable for COC due to parametrization. In addition, the PCFF and COMPASS force fields contain several terms, which correlate with each other. Therefore, the re-optimization of these force fields is difficult. In a previous study, we re-parametrized the Dreiding 2.21 force field for COC consisting of ethylene and norbornene [45]. Here, our focus is on property prediction for COC modified with methyl groups and propane units. For this purpose, we re-parametrized the Dreiding 2.21 force field further to make it suitable for the prediction of mechanical and thermal properties of modified COC by molecular dynamics simulations. Optical properties were investigated by ab initio methods.

2 Theory and computational details

The original and modified COC chains were studied with four polymer fragments. The COC consisted of norbornane or methyl norbornane and ethane or propane units. The applied polymer fragments were NENEENEE, N(Me)EN(Me), N(Me)PN(Me) and NPN units, where N is norbornane unit, E is ethane unit, Me is methyl unit and P is propane unit (Fig. 1).

Experimentally determined crystal structures were utilized as a support for the conformational analyses. Crystal structures containing similar polymer fragments to those in

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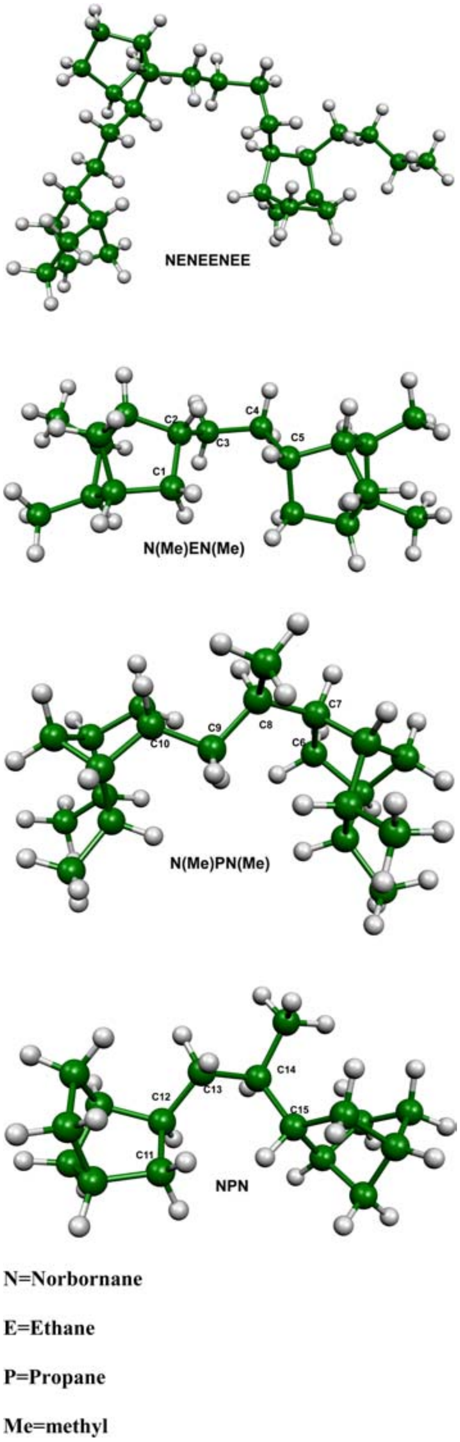

Fig. 1 Applied molecular fragments: NENEENEE, N(Me)EN(Me), N(Me)PN(Me) and NPN

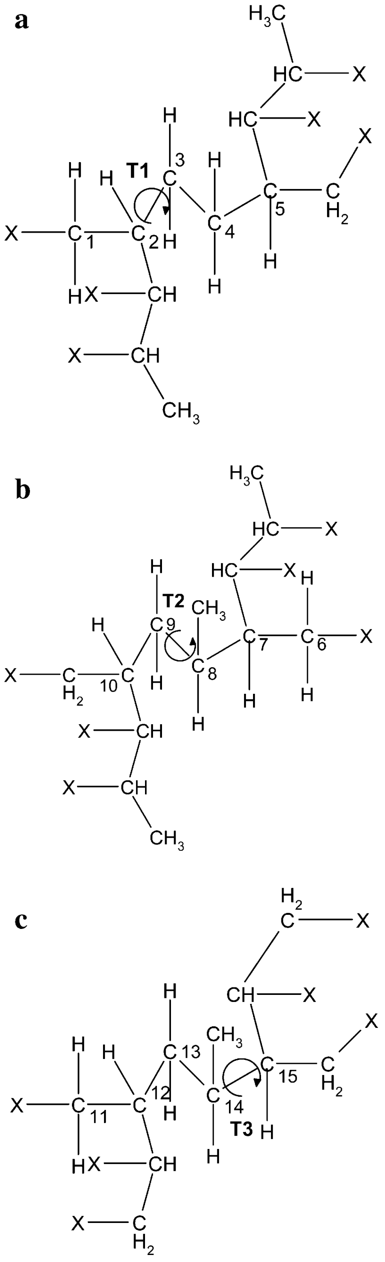

Fig. 2 Polymer fragments of modified COC in crystal structure search. **a** T1 of N(Me)EN(Me), **b** T2 of N(Me)PN(Me) and **c** T3 of NPN

the studied fragments were acquired from the Cambridge Structural Database [46]. Structures containing transition metals and structures that were part of a rigid ring were omitted. The search yielded 15 suitable crystal substructures: five for torsion T1(C1–C2–C3–C4) of N(Me)EN(Me), five for torsion T2(C7–C8–C9–C10) of N(Me)PN(Me) and five for torsion T3(C12–C13–C14–C15) of NPN. The applied structural units are shown in Fig. 2.

The refractive indexes of COC were determined by means of isotropic polarizibilities. The ab initio methods that were utilized were HF and B3LYP with 6-31G* and 6-311G** basis sets. The refractive indexes were calculated according to the Lorentz–Lorenz equation [21]. (Eq. 1), where N is particle density, *a* is isotropic polarizibility and *n* is the refractive index.

$$\frac{n^2-1}{n^2+2}=\frac{4\pi Na}{3} \qquad (1)$$

The Dreiding 2.21 force field was re-parametrized on the basis of conformational analyses. The geometry optimizations and conformational analyses were carried out by HF/3-21G and B3LYP/6-31G* methods using the Gaussian 03 program [47]. The parameters of the Dreiding 2.21 force field were modified to obtain the best fit with B3LYP/6-31G* calculations. The focus was on independent parameters (bond stretching, bond bending and torsion) of the force field, which do not affect other parameters of the force field.

Molecular dynamics simulations were carried out with the Cerius 2 program [48] with Dreiding 2.21 and modified Dreiding 2.21 force fields. Mechanical properties (bulk modulus (B), Young's modulus (Y) and Poisson's ratio (υ)) were determined by the second-derivative method [49]. The simulation cube contained five polymer chains and each chain contained ten monomers (Fig. 3).

The glass transition temperatures (T_g) were determined by NPT (constant particle number, pressure and temperature) molecular dynamics simulation. The temperature range was 300–600 K for N(Me)EN(Me) and 300–500 K for N(Me)PN(Me) and NPN. The simulation step was 1 fs and electrostatic interactions were calculated by utilizing the Ewald method with dielectric constant of 2.35. The simulations were run for 100 ps at all temperatures. Monitoring of a specific volume–temperature (V–T) curve enables prediction of the glass transition temperature (T_g). The break in the slope of the V–T curve indicates the location of the T_g. Error limits were derived from standard deviations.

3 Results and discussion

3.1 Conformational analyses and modifications of force fields

The N(Me)EN(Me) fragment contains two relevant torsions for conformational analysis, and the N(Me)PN(Me) and NPN fragments contain three. The conformational energy curves are presented in Fig. 4 for torsions T1(C1–C2–C3–C4) of N(Me)EN(Me), T2(C7–C8–C9–C10) of N(Me)PN(Me) and T3(C12–C13–C14–C15) of NPN, in which the original Dreiding 2.21 indicated most deviations from the ab initio calculations.

In torsion T1 of N(Me)EN(Me), the global minimum appeared at dihedral angle of 60.0° and the local minima at the points −60.0° and 180.0°. The global maximum appeared at dihedral angle of 0° and the other maxima at points −100.0° and 140.0°. All crystal structures were found at the global minimum point in agreement with ab initio calculations. In the case of torsion 2 of N(Me)PN(Me) and torsion 3 of NPN (Fig. 3), the global minima were at the point 180.0° and local minima at the points −60.0° and +60.0°. The potential energy curves determined by ab initio calculations were in good agreement with the crystal structure findings. The original Dreiding 2.21 force field failed in the potential energy description for torsion T1 of N(Me)EN(Me) in general and for torsion T2 of N(Me)PN(Me) between −180.0° and −0.0°.

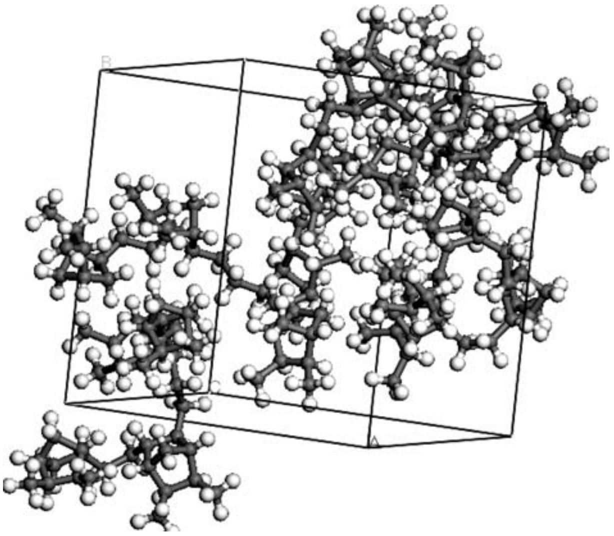

Fig. 3 The simulation cube of N(Me)EN(ME) type COC

To improve its performance, we re-optimized the force field parameters (modified Dreiding 2.21) to make them suitable for the utilized COC fragments. The bond-stretching and bond-bending parameters were obtained from the work of Ahmed et al. [27] and the torsion terms were re-optimized by producing the new parameters from B3LYP/6-31G* torsional behavior (Table 1). The torsion term of the Dreiding 2.21 force field is presented in Eq. 2. With all potential energy curves, agreement was obtained between modified Dreiding 2.21 and ab initio curves.

$$E_{\text{Torsion}} = \sum_{n} \frac{1}{2} V_n \{1 - \cos(\varphi - \varphi_0)\} \tag{2}$$

3.2 Prediction of mechanical and thermal properties by molecular dynamics simulations

The re-optimized Dreiding 2.21 force field was utilized for the prediction of mechanical and thermal properties of modified COC. Mechanical properties (bulk modulus (B), Young's modulus (Y), and Poisson's ratio (υ)) and thermal properties (glass transition temperature (T_g)) of modified COC were calculated by force-field-based molecular dynamics simulations with both modified and original Dreiding 2.21 force fields. Where available, experimental data was utilized as a support for the simulations. The results are listed in Table 2.

Table 1 The original and modified parameters of the Dreiding 2.21 force field for modified COC

Torsion (NEN) {T1 and T2}	Dreiding 2.21 (kcal/(mol Å^2))	Mod. Dreiding 2.21 (kcal/(mol Å^2))
V_1	0	0
V_2	2.0	1.82
V_3	0	4.48

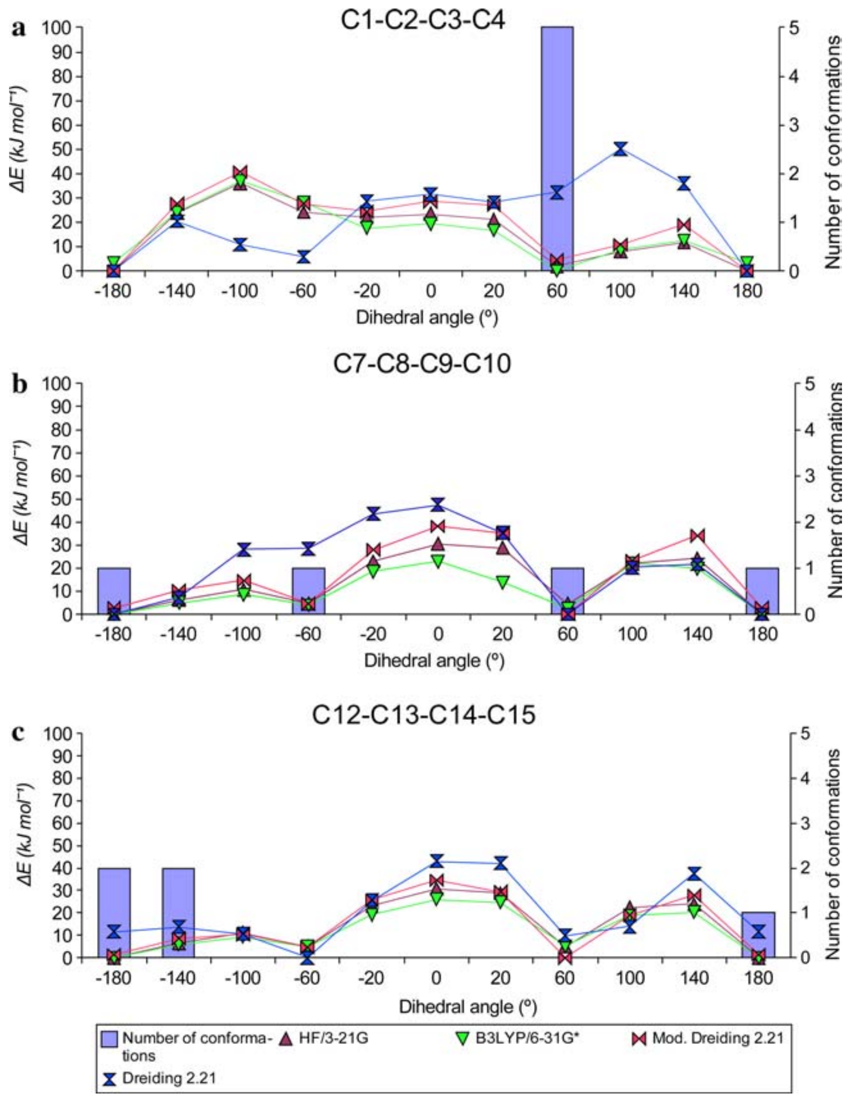

Fig. 4 Potential *energy curves* for modified COC. The *bar diagram* compares the hits of the *crystal structure* search with the calculated conformations. **a** T1 of N(Me)EN(Me), **b** T2 of N(Me)PN(Me) and **c** T3 of NPN

Table 2 Results of molecular dynamics simulations for modified COC

Property	COC type	Dreiding 2.21	Mod. Dreiding 2.21	Experimental [6,33]
B (GPa)	NEN	3.54 [45]	4.78 [45]	4.1–5.9
	N(Me)EN(Me)	2.26	5.20	
	NPN	5.95	5.43	–
	N(Me)PN(Me)	3.50	4.29	–
Y (GPa)	NEN	3.85 [45]	3.45 [45]	3.2
	N(Me)EN(Me)	2.80	4.64	–
	NPN	5.16	5.88	–
	N(Me)PN(Me)	4.08	3.98	–
ν	NEN	0.32 [45]	0.38 [45]	0.37–0.41
	N(Me)EN(Me)	0.38	0.33	–
	NPN	0.33	0.33	–
	N(Me)PN(Me)	0.31	0.34	–
T_g (°C)	NEN	277 ±14.5 [45]	227 12.9 [45]	200
	N(Me)EN(Me)	119 ±27.2	249 ±14.9	–
	NPN	49 ±25.2	121 ±11.4	131
	N(Me)PN(Me)	210 ±14.6	161 ±14.5	–

Table 3 Calculated isotropic polarizabilities for COC structures

Refractive index	HF/6-31G*	HF/6-311G**	B3LYP/6-31G*	B3LYP/6-311G**
NENEENEE	296.5	316.2	314.7	341.4
N(Me)EN(Me)	190.1	203.4	201.8	219.6
NPN	159.6	170.3	168.5	183.1
N(Me)PN(Me)	199.8	213.9	212.1	231.0
$[\text{NENEENEE}]_2$	444.9	474.1	474.2	515.7
$[\text{N(Me)EN(Me)}]_2$	294.1	313.9	312.7	339.4
$[\text{NPN}]_2$	253.6	269.9	268.9	291.1
$[\text{N(Me)PN(Me)}]_2$	313.9	335.3	335.1	364.0

Table 4 Calculated refractive indexes for COC structures

Refractive index	HF/6-31G*	HF/6-311G**	B3LYP/6-31G*	B3LYP/6-311G**	Experimental [6]
NENEENEE	1.444	1.479	1.476	1.524	1.530
N(Me)EN(Me)	1.440	1.476	1.472	1.521	–
NPN	1.406	1.437	1.432	1.475	–
N(Me)PN(Me)	1.439	1.475	1.470	1.520	–
$[\text{NENEENEE}]_2$	1.446	1.475	1.480	1.524	1.530
$[\text{N(Me)EN(Me)}]_2$	1.440	1.475	1.472	1.520	–
$[\text{NPN}]_2$	1.415	1.445	1.443	1.486	–
$[\text{N(Me)PN(Me)}]_2$	1.439	1.474	1.473	1.522	–

The bulk and Young's moduli were clearly higher for N(Me)EN(Me)-type than for NEN-type COC. This is due to methyl groups, which increase a stiffness of the polymer chains, thereby resulting in higher bulk and Young's moduli. In addition, the electropositive methyl groups can donate electron density to the backbone C–C bonds and strengthen the polymer chains. However, this effect is less important since the methyl groups do not locate near the backbone C–C bonds. The lower Poisson's ratio of N(Me)EN(Me) indicated that the material was also more rigid. The glass transition temperature of N(Me)EN(Me) was higher because the methyl groups hindered the movements of polymer chains.

An opposite trend was observed for N(Me)PN(Me) copolymer. The calculated bulk and Young's moduli were lower than in NPN copolymer (Table 2). The N(Me)PN(Me)-type COC contains several methyl groups and all methyl groups together affect as plasticizer agents by increasing cavity volumes of polymer chains. This results in lower bulk and Young's modulus values compared to NPN molecule, which contains only one methyl group. The slightly higher Poisson's ratio of N(Me)PN(Me) copolymer indicated greater flexibility of the material, likewise predicting lower values for Young's and bulk moduli. The glass transition temperature was higher for N(Me)PN(Me) due to the steric effect of the methyl groups. A similar trend was observed by Bergström et al. [32,50] in experiments with phenylnorbornene and indanylnorbornene.

Since polypropylene has a higher B, Y and T_g than polyethylene, NPN copolymer was expected to have higher B, Y and T_g than NEN copolymer. The bulk and Young's moduli of NPN were higher, while the Poisson's ratio was lower than the corresponding values of NEN. However, the T_g was an exception. According to Tritto et al. [30] this is due to the steric repulsion of the methyl groups of propylene units, which increases the cavity volume of the polymer chains, resulting in lower T_g. However, this phenomenon appears only, if the amount of norbornane units in polymer chains is less than 80%. Higher amounts of the norbornane units can increase T_g of NPN copolymer up to 260° C [33].

3.3 Prediction of optical properties by ab initio methods

Refractive indexes of both modified and non-modified COC were studied by ab initio methods. The refractive indexes of polynorbornane have earlier been studied by ab initio as well as semiempirical methods by Hasselwander et al. [21]who found ab initio methods to be useful for this purpose. Their larger basis set improved the calculated isotropic polarizabilities and refractive indexes significantly, and the best agreement with experimental value was attained by Sadlej [51] basis set. In our study, isotropic polarizabilites were calculated by HF and B3LYP methods with basis sets 6-31G* and 6-311G**. The isotropic polarizabilities are listed in Table 3. The refractive indexes were calculated from the isotropic polarizabilities with the Lorentz–Lorentz equation. The refractive indexes were determined at wavelength 589 nm and where available, experimental data were utilized as a check on the results. The calculated refractive indexes are listed in Table 4.

Experimental data were available only for the non-modified COC. In addition to the level of theory, the calculations of refractive index are sensitive to the basis set. The best agreement with the experimental refractive index was obtained by B3LYP/6-311G** method, which seems to produce a refractive index very close to experimental values. Increasing the number of repeating units from one to two has practically no effect. The modifications of COC did not change the refractive indexes significantly, except for the NPN copolymer for which the refractive index was lower. A plausible explanation for this is that the electron density of the NPN molecule is low and therefore, the isotropic polarizability is also low.

4 Conclusions

Mechanical and thermal properties of modified COC were studied by molecular simulations using a modified Dreiding 2.21 force field. The non-correlating parameters of the Dreiding 2.21 force field were optimized by searching for the best fit to the B3LYP potential energy curves. Crystal structures recovered from the Cambridge Structural Database were utilized to verify the correctness of the observed potential energy minima and maxima.

Addition of methyl groups to the norbornane rings of NEN-type COC clearly increased both bulk and Young's moduli. Apparently, the introduction of methyl substituents improve bulk and Young's moduli by increasing a stiffness of the polymer chains. The glass transition temperature increased as well, since the methyl groups hindered the movements of the polymer chains. Replacement of ethane with propane unit (NPN copolymer) in the COC chain increased the bulk and Young's moduli due to the higher stiffness of polymer chains. However, the glass transition temperature of the NPN copolymer was lower than that of the NEN copolymer because the steric repulsion of the methyl groups of the propane increases the cavity volume of the polymer chains, and thereby lowers the T_g.

The performance of various ab initio methods for the prediction of refractive indexes of modified and non-modified COC was studied. The calculations of the refractive index were sensitive to the applied basis set and level of theory. A good match with experimental data was obtained with the B3LYP/6-311G** method. The effects of the structural modifications were insignificant, except for the NPN copolymer, which had a lower refractive index.

References

1. Marathe S, Mohandas TP, Sivaram S (1995) Macromolecules 28:7318
2. Marathe S, Sivaram S (1994) Macromolecules 27:1083
3. Harrington BA, Crowther DJ (1998) J Mol Cat A 128:79
4. Kaminsky W (1999) Rapra Rev Reports 10:28
5. Kaminsky W, Laban A (2001) Appl Catalysis 222:47
6. Land HT, Niedernberg D (1995) Kunststoffe 85:1048
7. Alt FP, Heitz W (1998) Acta Polym 49:477
8. Ruchatz D, Fink G (1998) Macromolecules 31:4681
9. Kaminsky W (1994) Catal Today 20:257
10. Herfert N, Montag P, Fink G (1993) Macromol Chem 194:3167
11. McKnight AL, Waymouth RM (1999) Macromolecules 32:2816
12. Kaminsky W, Bark A, Arndt M (1991) Macromol Chem 47:83
13. Kaminsky W, Bark A, Arndt M, Beulich I (1997) Polym Mater Sci Eng 76:18
14. Arndt M, Beulich I (1998) Macromol Chem Phys 199:1221
15. Goodall BL, McIntosh LH, Rhodes LF (1995) Macromol Symp 89:421
16. Young M, Chang W, Ma CM (2003) Eur Polym J 39:165
17. Arndt M, Beulich I (1999) Macromolecules 32:7335
18. Provasoli A, Ferro DR, Tritto I, Boggioni L (1999) Marcomolecules 32:6697
19. Rische T, Waddon JA, Dickinson LC, MacKnight WJ (1998) Macromolecules 31:1871
20. Chu PP, Huang JW, Chang CF, Fan YS (2000) Polymer 41:401
21. Haselwander TFA, Heitz W, Krügel SA, Wendorff JH (1996) Macromol Chem Phys 199:3435
22. Mastryukov VS, Chen K, Allinger NL (2001) J Phys Chem 105:8526
23. Ahmed S, Allen SA, Kohl P, Ludovice PJ (1996) Soc Plast Eng 54:2179
24. Shaw RA, Ibrahim N, Wieser H (1989) Can J Chem 67:535
25. Shaw RA, Castro C, Dutler R, Raul A, Wieser H (1988) J Chem Phys 89:716
26. Chung W, Chang J, Yoon DY (2001) Polym Mater Sci Eng 85:626
27. Ahmed S, Bidstup SA, Kohl PA, Ludovice PJ (1998) J Phys Chem B 102:9783
28. Haselwander TFA, Heitz W, Krügel S, Wendorff JH (1997) Macromolecules 30:5345
29. Grove NR, Kohl PA, Allen SAB, Jayaraman S, Shick R (1999) J Polym Sci B 37:3003
30. Boggioni L, Bertini F, Zannoni G, Tritto I, Carbone P, Ragazzi M, Ferro RD (2003) Macromolecules 36:882
31. Carbone P, Ragazzi M, Tritto I, Boggioni L, Ferro DR (2003) Macromolecules 36:891
32. Bergström C (2001) Acta Polym Scan 281:2
33. Henschke O, Köller F, Arnold M (1997) Macromol Rapid Commun 18:617
34. Bauer HD, Ehrfeld W, Harder M, Paatzsch T, Popp M, Smaglinski I (2000) Synthetic Met 115:13
35. Huang W, Chang F, Chu PP (2000) Polymer 41:6095
36. Maple JR, Hwang MJ, Stockfisch TP, Dinur U, Waldman M, Ewig CS, Hagler, AT (1994) J Comput Chem 15:162
37. Peng Z, Ewig CS, Hwang MJ, Waldman M, Hagler AT (1997) J Phys Chem A 101:7243
38. Sun H (1994) J Comput Chem 15:752
39. Sun H (1994) Macromolecules 26:5924
40. Sun H, Mumby SJ, Maple JR, Hagler AT (1994) J Am Chem Soc 116:2978
41. Sun H (1995) Macromolecules 28:701
42. Sun H, Mumby SJ, Maple JR, Hagler AT (1995) J Phys Chem B 99:5873
43. Sun H, Rigby D (1997) Spectrochim Acta (A) 53:1301
44. Sun H (1998) J Phys Chem B 102:7338
45. Katajisto J, Linnolahti M, Pakkanen TA (2004) J Phys Chem B 108:2168
46. Allen FH (2002) The Cambridge structural database: a quarter of a million crystal structures and rising, B58, 380
47. Frisch MJ, Trucks GW, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Vreven T, Kudin KN, Burant JC, Millam JC, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski J, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski BB, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gozalez C, Pople JA (2003) Gaussian 03. Revision B.01., Gaussian Inc., Pittsburgh
48. Accelrys Inc. (2001) Cerius 2., Version 4.6., Accelrys Inc.
49. Fan CF, Cagin T, Chen ZM, Smith KA (1994) Macromolecules 27:2383
50. Aitola E, Repo T, Bergström C, Leskelä M (2002) J Appl Polym Sci 84:2743
51. Sadlej AJ (1988) Collect Chech Chem Commun 53:1995