Polymer Bulletin 45, 397–404 (2000)

Polymer Bulletin

Glass transition temperature and thermal degradation of N-2-acryloyloxyethyl phthalimide copolymers

M. Fernández-García (✉), J. L. de la Fuente, E. L. Madruga

Instituto de Ciencia y Tecnología de Polímeros (C.S.I.C.), Juan de la Cierva 3,
28005-Madrid, Spain
e-mail: ictf310@ictp.csic.es, Fax: 34-91-5644853

Received: 30 May 2000/Revised version: 19 October 2000/Accepted: 19 October 2000

Summary

Copolymers of methyl methacrylate, MMA, with N-2-acryloyloxyethyl phthalimide, AEP, have been prepared by free radical polymerization. Glass transition temperatures, T_g; and thermal degradation of homo and copolymers have been determined by differential scanning calorimetry and by thermogravimetric analysis. Johnston's equation, which considers the influence of monomeric units' distribution on the copolymers glass transition temperature, has been used to explain the T_g behavior. The T_{g12} has been calculated by the application of Johnston=s equation, given a value sensibly lower than the corresponding homopolymers $T_{g.}$ The thermal stability of copolymers depends on the composition of the copolymer.

Introduction

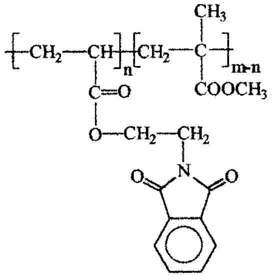
It is well known that polymer properties are controlled by molecular properties, such as, molecular weight, molecular weight distribution, chemical composition and stereochemical distribution of copolymer chain, degree of crosslinking, etc. which, in turn, are a reflection of the kinetic history of the reactions occurred during its formation.

Polymer glass transition temperature -representing the molecular mobility of the polymers chains- is an important phenomenon that influences the material properties and potential applications of a given polymer. In general, the more hindered the rotation around backbone carbon-carbon bonds, because of large substituent groups, the higher the glass transition. However, the opposite is observed in the case of flexible side chain, such as alkyl groups, which act more like plasticizers and, therefore, lower the glass transition temperature.

Likewise, the thermal stability of polymeric materials is an important physical property, which conditioned many applications. It is important to know the thermal degradation temperature to ensure a safety service temperature, which is possible to maintain their properties. These properties can be extremely affected by the presence of particular sequences of comonomers. It is also well known that polymers with methacrylic acid or anhidride [1][2], acrylic acid [2] or a rigid imide ring [3][4] structure provide structural integrity.

Taking into account that the monomer disposition in a copolymer chain is determined by the kinetic event, it is essential to consider not only intermolecular microstructure (average and cumulative chemical composition) but also intramolecular microstructure (sequence distribution), since these parameters play a important role in the understanding of relation between molecular structure and properties.

In this study, the determination of glass transition temperature for methyl methacrylate- N-2-acryloyloxyethyl phthalimide copolymers (see Scheme 1) are analyzed considering its dependency with the inter and intramolecular structure of the copolymer chain. Furthermore, the thermal stability of these copolymers is studied.



Scheme 1. Methyl methacrylate- N-2-acryloyloxyethyl phthalimide copolymers

Experimental

Materials: The purification and synthesis of methyl methacrylate, MMA, (Merck), N-2-acryloyloxyethyl phthalimide, AEP, was described elsewhere [5]. 2.2'-Azobisisobutyronirile, AIBN, (Fluka) was purified by successive crystallization from methanol. Dimethylformamide (Merck) was distilled twice over P_2O_5 at reduced pressure and stored in dark glass bottles over dried molecular sieves, 4Å.

Copolymers were prepared by free radical polymerization of mixtures of both monomers with different compositions, in dimethylformamide at 60°C. The concentration of initiator was $5\cdot 10^{3}$ mol/l in all these cases and the total monomer concentrations were 1 mol/L. The copolymerization experimental details were reported previously [5].

Homopolymerization of monomers were performed in the same experimental conditions as copolymerization.

From the previous kinetic data [5], we can assure that molecular mass of copolymer is large enough to not influence the T_g values.

Glass transition temperatures: Glass transition temperatures were measured using a Differential Scanning Calorimeter, Perkin Elmer DSC/TA7DX, PC series with a water circulating system. The temperature scale is calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples (~10 mg) weighed to ±0.002 mg with an electronic autobalance (Perking Elmer AD4) were scanned at 10 deg/min, cooled at 320 deg/min and then, heated again at 10 deg/min under dry nitrogen (20 cm^3/min).

The actual value for the glass transition temperature T_g was estimated from the second run as the temperature at the midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The current value is the average for several measurements realized for each composition. The values estimated according to this criterion, when they are compared with those obtained following other procedures, may be apparently higher. In our case, this is also due in part to the heating rate employed (10 deg/min).

Thermal degradation: A Perkin-Elmer TGA-7 instrument was used for the thermogravimetric measurements. The instrument was calibrated both for temperature and weight by the usual methods. Non-isothermal experiments were performed in the temperature range from 30-600°C at heating rate of 10 deg/min. The average sample size was ~4 mg, powder, and the dry nitrogen and the flow rate was 20 cm^3/min.

Results and discussion

Methyl methacrylate, MMA, was copolymerized with N-2-acryloyloxyethyl phthalimide, AEP, in dimethylformamide solutions at 60°C and using AIBN as initiator and molar fraction of MMA in the feed, f_{MMA}, between 0.11_1 and 0.80_0. Methyl methacrylate molar fractions in the copolymer chain, F_{MMA}, were obtained by ^{1}H-NMR. The reactivity ratios were calculated by applying the Mayo-Lewis terminal model [5], being $r_{MMA}= 3.07$ and $r_{AEP}= 0.30$, respectively.

Physical properties of a copolymer are fundamentally determined by its glass transition temperature. Originally, the copolymers T_g were described by simple additive relations [6][7], based on free volume theories [8][9][10], thermodynamic theories [6], which did not take into consideration the sequence distribution of the monomer units and the effect of their compatibility on steric and energetic interactions. The free volume theory developed by Fox and Flory [8] suggests that the glass transition occur when the free or unoccupied volume of the material reaches a constant value and does not decrease further as the material is cooled below its T_g. A thermodynamic theory, proposed by Gibbs and DiMarzio [6], is based on the change of material configurational entropy as a function of temperature. At equilibrium it postulates that the configurational entropy, Sc, equal zero at the glass transition. However, these linear relationships often failed in predicting accurate glass transition temperatures of copolymers, since they neglected the effect of the chemical nature and organization of the monomers on the mobility of a polymer chain [11]. Several models were therefore proposed [11][12][13] that differentiated between homo (M_1-M_1, M_2-M_2) and heterolinkages (M_1-M_2 or M_2-M_1), recognizing the significant effect of monomer arrangement on glass transition temperature, such that both negative and positive deviations from the linearity may be predicted. The relations proposed by Barton [11], Uematsu and Honda [13], Hirooka and Kato [14], Furukawa [15] and Suzuki *et al.* [16] may be considered as extensions of the Gibbs-DiMarzio [6] relation, whereas the approach by Johnston [10] is based on the Fox equation [8]. A third relation, developed by Couchman [12], is based on mixed-system entropy and was also able to predict composition-dependent glass transition temperatures for a variety of systems.

Among all of these, the ones derived by Johnston, Barton or Couchman which correlate T_g to the dyad distribution in the instantaneous copolymer molecules, exhibit better agreement with experimental T_g's [17][18]. In this work we are going to use the Johnston's equation which is based on the free volume concept and the inter-intramolecular composition of the copolymer. The description of Johnston's model is as follow:

Johnston's equation [10] assumes that M_1M_1, M_1M_2 or M_2M_1 and M_2M_2 dyads have their own glass transition temperature, with the overall T_g of a copolymer described by the following expression:

$$\frac{1}{T_g} = \frac{w_1 P_{11}}{T_{g11}} + \frac{w_2 P_{22}}{T_{g22}} + \frac{w_1 P_{12} + w_2 P_{21}}{T_{g12}} \qquad \textbf{(1)}$$

in which w_1 and w_2 are the weight fractions of monomeric units in the main chain, P_{11}, P_{12}, P_{21} and P_{22} are the probabilities of having various linkages, which can be calculated considering the Mayo-Lewis terminal model by using the monomer feed composition and the monomer reactivity ratios [19]. T_{g11} and T_{g22} are the glass transitions of the respective homopolymers and T_{g12} is the supposed glass transition for the alternating sequence M_1M_2 or

M_2M_1.

To apply the Johnston theory it is necessary to determine the glass transition temperature of a strictly alternating copolymer, T_{g12}. In this case, T_{g12} for MMA-AEP copolymers is unknown, but it can be calculated from our own experimental values (Table 1): T_g of pMMA, T_g of pAEP (T_{g11} and T_{g22}, respectively) and T_g's of a copolymers series of varied composition obtained at low conversion. A value of 357.2K is found for AEP T_g, almost 110K higher than the alkyl homologue, ethyl acrylate [20], which indicates that the rigid imide ring hinders the rotation around the bonds. A linearized form of the equation (1) is used to determine T_{g12}. As it can be observed, in Figure 1 the experimental data produce a very good straight line, with the T_{g12} value 325.3K.

Table 1. Glass transition temperatures and the maximum rate temperature of weight loss, T_{max}, of MMA-AEP copolymers obtained in dimethylformamide solution at 60°C

f_{MMA}	F_{MMA}	Conversion (%)	T_g (K)	T_{max} (K)
0.00_0	0.00_0	7.3	357.2	702.7
0.11_1	0.30_0	5.8	344.8	696.1
0.13_6	0.36_0	3.6	343.2	696.8
0.15_9	0.39_0	3.9	346.0	697.5
0.20_0	0.42_0	5.5	346.7	695.7
0.37_6	0.64_4	4.5	348.8	694.7
0.40_0	0.70_0	4.2	350.4	694.8
0.41_9	0.72_5	4.7	350.6	690.0
0.47_6	0.71_0	5.1	352.7	686.1
0.60_0	0.85_0	3.1	358.8	687.0
0.80_0	0.90_5	4.2	374.0	681.4
1.00_0	1.00_0	6.3	393.2	665.7

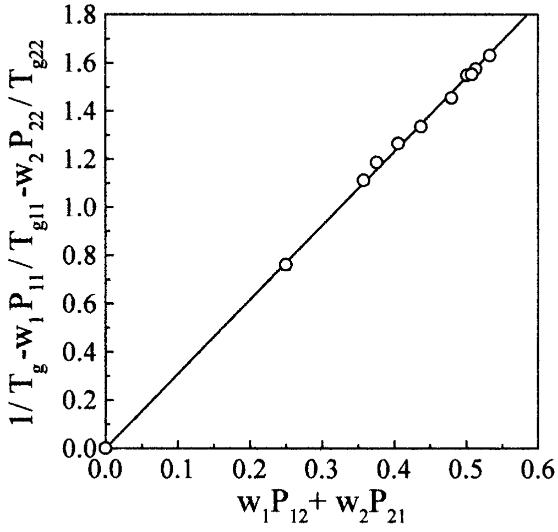


Figure 1. Plots of the glass transition temperatures of MMA-AEP copolymers according to the linearized expression of Johnston [10]

It is important to remark that within experimental accuracy, T_{g12} (MMA-AEP or AEP-MMA link) has lower value than T_{g11} (MMA-MMA link) and T_{g22} (AEP-AEP link). Moreover, the copolymer T_g presents a minimum at 0.26 methyl methacrylate weight molar fraction in the copolymer chain, which correspond to a F_{MMA}=0.46.

Considering the T_{g12} value found and according to the Johnston's equation [10], the curve of Figure 2 is drawn. DSC curves for different MMA-AEP copolymers are shown in Figure 3. The dependence on T_g with methyl methacrylate weight molar fraction, w_{MMA}, in the copolymer is displayed in Figure 2. As can be observed, when w_{MMA} is less than 0.15 the T_g decreases markedly, then there is a range placing from 0.22 to 0.35 where the T_g is almost unchangeable, reaching a minimum at w_{MMA} around 0.26. For w_{MMA} from 0.26 to 0.5 the T_g increases smoothly, however, for w_{MMA} higher than 0.5 the increases is considerably and only for w_{MMA} higher than 0.60 the T_g is between both homopolymers T_g. This behavior has been also observed in copolymers with imide-containing monomers [3]

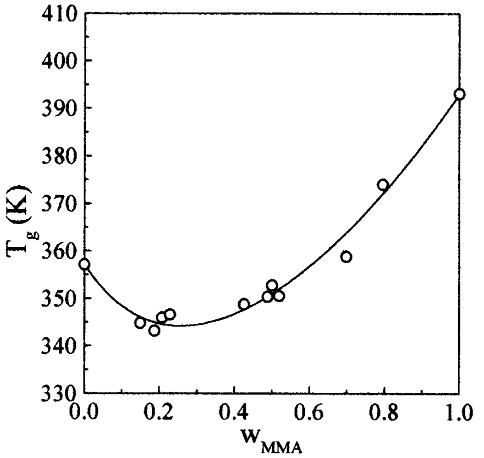


Figure 2. Glass transition temperatures of MMA-AEP copolymers as a function of methyl methacrylate weight molar fraction in the copolymer chain

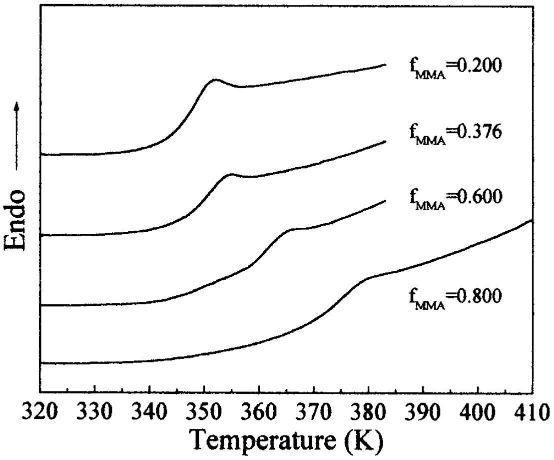


Figure 3. DSC curves of different MMA-AEP copolymers

The variation of copolymers T_g as a function of copolymer chain composition could be explicated considering the influence of the copolymer microstructure on the glass transition temperature. From monomer feed composition, monomer reactivity ratio values and using Bernoulli's statistic, it is easy to calculate the formation probabilities of M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 dyads as a function of monomer molar fraction in the feed. Knowing this data, it is trivial to determine the dyads molar fraction as a function of weight fraction of monomer unit.

In Figure 4 are represented the calculated dyads molar fractions for this system. As can be observed, at w_{MMA} lesser than 0.15 the AEP-AEP, (22), dyad concentration is higher than 50%, which means that the contribution of T_{g22} to the overall copolymer T_g is predominant. However, due to the contribution of T_{g12}, which, as has been pointed out, is lower than the homopolymers T_g, the T_g goes to inferior temperatures. From w_{MMA} between 0.22 and 0.35 the sum of MMA-AEP, (12), and AEP-MMA, (21), is practically 50%. Therefore, in this range the overall copolymer T_g does not change significantly. For w_{MMA} higher than 0.50 the

MMA-MMA dyad concentration is higher than 50%, then, the copolymer T_g increases notably.

On the other hand, Hirooka *et al.* [14] have observed the T_g for dyads, T_{g12}, calculated from the T_g of a series of copolymers of varied composition, did not always correspond with that of the chemically synthesized alternating copolymer. This deviation depends on the type of T_g-composition relationship of the statistical copolymer. T_g of a pure alternating copolymer should be higher, lower or similar to that T_g estimated from T_g-sequence distribution when the T_g-composition curve for statistical copolymer is convex, concave or linear, respectively.

Tonelli [21] has used the conformational entropy as a characterizing parameter for the polymer intramolecular chain flexibility. Deviations positive, negative or no deviation from bulk additive, namely T_{g12}, estimated from T_g -sequence distribution behavior are produced when the conformational entropy for a given copolymer chain is lower, higher or similar, respectively, to the weighed sum of entropies calculated for the constituent homopolymer chains.

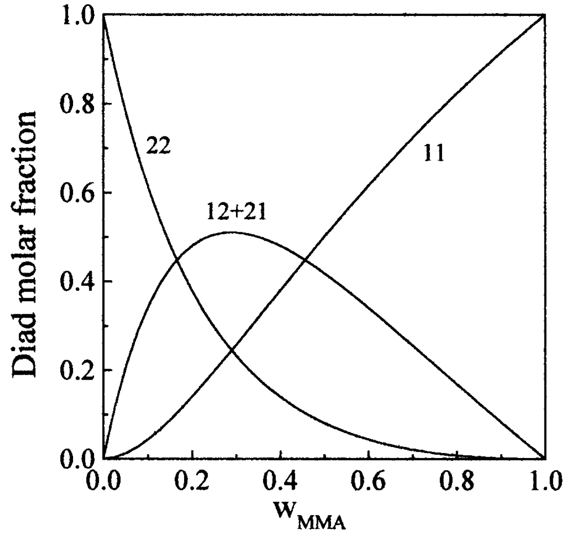


Figure 4. Dyad molar fractions *versus* methyl methacrylate weight molar fraction in the MMA-AEP copolymer chain

Moreover, the T_g of the polymer is related to the chain flexibility and this parameter is, to a large extension, a reflection of the rotational barrier about the bond linking two monomer units. Depending on the rotational barrier of heterolink bond being similar, higher or lower than the averaged rotational barrier of homolink bond, the copolymer T_g-composition behavior will be linear or show positive or negative deviations from the linearity [18]. Hirooka *et al.* [14] have proposed that the difference between the average $\overline{T_g}$, $\overline{T_g}=(T_{g11}+T_{g22})/2$, and the supposed glass transition temperature of an alternating copolymer T_{g12} may be regarded a measure of heterolink stiffness. In this work the average $\overline{T_g}$ is 375.2K whereas a lower value of T_{g12}, 325.3K, is obtained using the Johnston's equation [10]. This fact indicated that this system has heterolink stiffness lower than the average of homopolymer links and lower than the two homopolymers links. Consequently, negative deviation from the linearity in the T_g-composition observed in Figure 2 is expected. The cause of this behavior is not clear since the chain flexibility not only depends on the rotation barrier but also on the chain packing, side chain stiffness, dipole interactions, etc. Due to the lower T_{g12} obtained seems feasible that the chain packing in the copolymers presents lower energy that the chain packing in the homopolymers.

Taking into account all these features, a good agreement between experimental and theoretical values is found, indicating that the Johnston's equation and terminal model of Mayo and Lewis through reactivity ratios may be used to describe the dependence between experimental glass transition temperature of MMA-AEP copolymers and their sequence distribution.

The thermogravimetric curves, TGA, and its corresponding differential, DTG, of the different copolymers under nitrogen at 10°C/min are shown in Figure 5. The maximum rate temperatures of weight loss, T_{max}, for each copolymer are gathered in Table 1. Having T_{max} of the main peak as reference parameter of stability, the thermal stability of copolymers increases as f_{MMA} decreases.

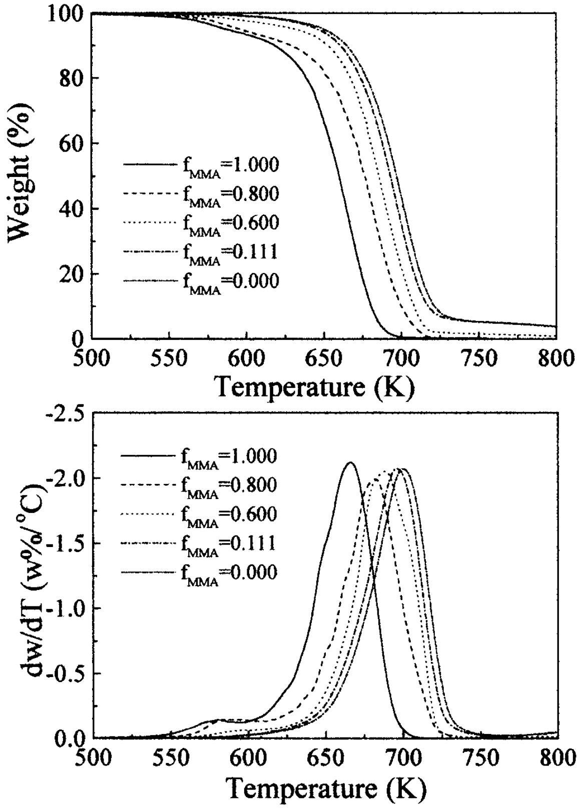


Figure 5. TGA and DTG curves of MMA-AEP copolymers

It is well known that unsaturated linkages at the end of polymer chains, as well as head-to-head linkages, contribute to the polymer instability [22]. Depending on the chemical mechanism of the termination reaction in free radical polymerization, unsaturated linkages at the end of polymer chain (disproportion mechanism) or head-to-head linkages (combination mechanism) may be produced. Then, the knowledge of the ratio between the termination reactions produced by disproportion and combination is indispensable to the understanding the thermal stability of homo and copolymer obtained by free radical mechanism. It is

commonly accepted that the termination reaction in poly(methacrylates) is mainly due to disproportion, while that in the case of poly(acrylates) is due to combination [23].
As it can be seen, the thermal degradation of copolymers with high methyl methacrylate molar fraction shows similar behavior than that for poly(methyl methacrylate). DTG curves exhibit two peaks, the first one is attributed to the degradation end-initiated from the vinilydene end groups and the second one corresponds to the main chain random scission. This fact is in agreement with several authors [22][24] and also with that the termination reaction in the pMMA is due to disproportion, since the peak corresponding to the relative concentration of head-to-head linkages is insignificant and only the peak corresponding to unsaturated ends appears. As f_{MMA} decreases the decomposition of copolymer is produced in a single step, as occurs in pAEP, indicating that the thermal degradation is principally produced by random main chain scission. A decrease of MMA increases the amount of growing radicals ending in acrylate unit and then, the termination step is mainly produced by combination. However, in the acrylate, the head-to-head linkages do not seems to produce higher steric effects could induce instability at lower temperatures.

Acknowledgements. This research has been supported by The Comisión Interministerial de Ciencia y Tecnología (CICYT), (MAT97-682). Dr. M. Fernández-García is grateful to the Comunidad Autónoma de Madrid for her financial support.

References

1. Cerovecki Z, Kovacevic V, Besic Z, Stanojevic D, (1990), Angew. Makromol. Chem. 176/177:133
2. Switala-Zeliazkow M, (1993), Makromol. Chem. 194:1505
3. Staubli A, Mathiowitz E, Langer R, (1991), Macromolecules, 24:2291
4. Pyradi TM, Alasli NJ, (1989), J. Polym. Sci. (A) Chem., 27:2491
5. de Abajo J, Madruga EL, San Román J, de la Campa JG, Guzmán J, (1992), Polymer, 33:1090
6. Gibbs JH, DiMarzio EA, (1963), J. Polym. Sci. Part A-1, 1417
7. Fox TG, (1956), Bull. Am. Phys. Soc. 1:123
8. Fox TG, Flory PJ, (1950), J. Appl. Phys. 21:581
9. Gordon M, Taylor JS, (1952), J. Appl. Chem. USSR, 2:492
10. Johnston NW; (1976), J. Macromol. Sci. Rev. Macromol. Chem., C-14:215
11. Barton JM, (1970), J. Polym. Sci. C., 30:573
12. Couchman PR, Karasz FR, (1978), Macromolecules, 11: 117
13. Uematsu I, Honda K, (1975), Rep. Prog. Polym. Phys. Jpn., 8:111
14. a) Hirooka M, Jabunchi H, Iseky J, Nakai Y, (1968), J. Polym. Sci., A1. 6:1381 b) Hirooka M, Kato T, (1974), J. Polym. Sci. Polym. Lett., 12:31
15. Furukawa J, (1975), J. Polym. Sci. Polym. Symp., 51:105
16. Suzuki H, Kimura N, Nishio Y, (1996), J. Therm. Analysis, 46:1011 and their papers.
17. Fernandez-Garcia M, Gonzalez-Lopez MMC, Barrales-Rienda JM, Madruga EL, Arias C, (1994), J. Polym. Sci. Polym. Phys., 32:1191
18. MacEwen IJ, Johnson AF, (1985) in Alternanting Copolymers, JMG Cowie (ed.), Plenum Press, New York
19. Harwood HJ, Ritchey WM, (1964), J. Polym. Sci., B-2:601
20. Sunita ASB, (1993), Makromol. Chem, 194:1707
21. Tonelli A, (1977), Macromolecules, 10:716
22. Kashiwagi T, Inaba A, Brown JE, Hatada K, Kitayama T, Masuda E, (1986), Macromolecules, 19:2160
23. Moad G, Solomon DH, (1995) in "The Chemistry of Free Radical Polymerization", Elsevier Science, Ltd., Oxford, UK.
24. Hurley SL, Mittleman ML, Wilkie CA, (1993), Polym. Degrad. Stability, 39:345