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Nanoscale cooperativity on a series of statistical methacrylates copolymers with electron donor–acceptor pendant groups

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Abstract Standard and StepScan DSC studies have been performed on a series of statistical methacrylate copolymers with electron-donor and electron-acceptor pendant groups that form intramolecular electron transfers. From standard DSC analysis we concluded that glass transition temperature slowly increased with increasing electron-acceptor monomeric moiety ratio up to 0.5 in the main chain. Using StepScan DSC method we calculated the size and volume of cooperative rearranging region as well mean temperature fluctuation at glass transition temperature. It was estimated also the average number of monomer units in the cooperative rearranging region. All parameters were calculated according to the method proposed by Donth based on Heat Capacity Spectroscopy. The results show that the presence of intermonomeric electron transfers decreased the chain mobility, as well as the cooperativity of relaxation processes of these structures in the glass transition range. This is reflected by minimal values of these parameters around 0.4 ratio of copolymer composition. Such behavior is similar to that of crosslinked or confined systems (e.g., nanocomposites, thin films) that have reduced chain mobility.

Keywords Cooperative rearranging region · Glass transition · Intramolecular electron transfers · StepScan DSC

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Introduction

Despite of practical importance of T_g value, glass transition is not completely understood, namely if it is a pure kinetic process [1, 2] or it has only a thermodynamic behavior [3]. This is a reason for that glass transition still remains an intensively discussed issue. Most of researchers in the field consider that glass transition involves cooperative relaxation features, all of them agreeing both on kinetic and on thermodynamic behavior.

Adam and Gibbs [4] postulated the existence of cooperative rearranging region (CRR) as the smallest volume in material that at a given temperature can undergo rearranging independently of another neighboring regions. They proved that a cooperativity effect of rearranging regions is correlated with a thermodynamic behavior of glass transition. Therefore, the study of CRR could improve the understanding of the relaxation processes in amorphous materials at temperatures close to the T_g value. Thus, glass transition process could be evaluated in terms of cooperatively rearranging regions (CRR).

The CRR size is identified with the characteristic length of glass transition (ξ_α) that could be considered as an intrinsic parameter of the material. This parameter, ξ_α (or CRR size), was calculated for the first time by Donth in his dedicated study [5], based on Heat Capacity Spectroscopy (HCS) experiments. Moreover, he proposed an interpretation of CRR in terms of thermodynamic fluctuation model of small volume in material based on configurational entropy fluctuations. Such small volume that is named as sub-system is assigned to a local cubic nanometer size volume in amorphous materials. Later, Sillescu had same supposition in his review [6] based on configurational entropy and dynamic heterogeneity of such sub-system. According to his conclusions, more available conformational states are possible only if CRR is large enough. Sillescu connect the CRR term to dynamical heterogeneity over a sub-system with thermodynamic fluctuations.

CRR in glass-forming materials is described by Donth as a fluctuating space of a very small CRR volume (V_α) that is related to CRR size as $V_\alpha = \xi_\alpha^3$ [5]. The term "fluctuating" refers to a thermal fluctuation of CRR in glass transition range. Mean thermal fluctuation (noted as δT) could also be considered as an intrinsic parameter of glass transition that is responsible for changes in CRR volume due to changes of conformational entropy. These changes generate the rearranging processes of monomeric units, short parts, or branches of main chain in polymers by cooperative motions, independently of their neighboring regions. The CRR can be described as the volume of material with autonomy of relaxation processes induced by thermal fluctuations. According to Richert [7], CRR is as specific region which have a local relaxation time, therefore an amorphous polymer will have a very large number of CRR, each one with its own mobility and dynamic given by specific internal rearrangements. These rearrangements depend on the chemical nature of monomeric units, as well as on the particular steric hindrances induced by structure development at different levels by various ways (crystallization, blending, filler adding, thin film formation).

The values of CRR size were estimated in many works by different experimental techniques such as ^{1}H-NMR [8, 9], calorimetry [5, 10], atomic force microscopy [11], dielectric spectroscopy [12, 13] as well as by theoretical evaluation from molecular dynamic simulations [14, 15]. Most authors agree on similar range of CRR size, between 1 and 5 nm. In most of works, the size of CRR is proved to increase as temperature decreases. One interesting work has been published on direct observation of molecular cooperativity by probing dielectric fluctuation at nanoscale in glass transition range [16].

Many works were focused on the evolution of ξ_α with different chemical modifications or structural parameters for various polymeric materials. Results come to explain the role of cooperative rearranging processes on structural dynamics in material near T_g value. Thus, the value of ξ_α was correlated to the cross-link density in polymer networks [17, 18], with confination degree in nanostructured polymeric materials [19, 20] or with fragility index for large series of different glass-forming materials [21]. Some works estimated the variation of ξ_α with degree of crystallinity in PLLA [22], domains of microphases in polyurethanes [23], or filler content in polymer-based nanocomposites [24–27]. Relative recent studies report the variation of ξ_α with the anisotropy in PLLA [28], or in drawn PET [29, 30]. A new study investigates the effect of curing on nanoconfinement by monitoring the ξ_α value [31].

The characteristic CRR size and volume at glass transition can be evaluated from dynamic calorimetry experimental data using the method proposed by Donth based on thermodynamic fluctuation theory applied to glass transition [5]. The equation used for calculations of ξ_α from dynamic calorimetry derived from thermodynamic definitions proposed by Adam and Gibbs. Most authors have measured this parameter by DSC [5, 21, 31–33] and MDSC [21, 23, 29, 30]. Heat Capacity Spectroscopy is a relative complex technique that was also used for determination of ξ_α [5, 32, 34], because it can minimize the errors in experimental data.

StepScan DSC, as a relatively new calorimetric method, can give similar results to those obtained by other methods of MDSC group techniques. By this method it is possible to split a global calorimetric signal in two signals that can be associated to the two processes given by the MDSC method: a fast one (known as *in phase* signal, *reversible* part, *thermodynamic* or *storage* C_p process) and a slow one (denoted as *out of phase* signal, *irreversible* part, *kinetic* or *loss* C_p process) [35]. Experimentally it was found that the thermal history does not affect the thermodynamic response of the signal at glass transition [36, 37], but it does affect its kinetic response that is represented by exothermic changes during cooling or, opposite endothermic changes during heating through glass transition temperature range. Perkin Elmer (USA) developed the StepScan DSC method [38] that is a simplified method of the well-known MDSC technique [39]. The temperature program in StepScan DSC consists of a number of cycles including short periodic dynamic heating/cooling steps followed by isothermal steps. This is different to MDSC methods where a sinusoidal temperature program overlaps on linear heating/cooling. StepScan DSC gives similar information without need of complex Fourier transformation for deconvolution of heat capacity data as used by MDSC. StepScan DSC was used in many works as a general thermal analysis method of glass transition process [37, 39, 40], in studies of multiple melting processes in polymers [41, 42], or for studying thermal history effects [43], even on crystallization kinetic [44].

StepScan DSC was also used as a suitable analysis method for calculation of CRR size, CRR volume and thermal fluctuation interval. Up to now these parameters were calculated by this method for crosslinked PS and PMMA [45], showing that CRR size decreases as the crosslink density increase, this variation depending on the chemical structure. In another work the CRR size was estimated for rod-like capsules with crosslinked PS as shell, the confinement effect being discussed in function of CRR size [46].

The main purpose in this study is to calculate CRR size and volume, also to estimate the number of monomeric units inside CRR (noted as N_α) and mean fluctuation temperature (δT) at glass transition for a series of statistical methacrylate copolymers with pendant electron-donor and electron-acceptor groups using experimental data results from StepScan DSC measurements in glass transition range. StepScan method was used because it offers direct access to C_p and its variation with temperature during glass transition while this is difficult to obtain by standard DSC. We also tried to find a correlation between these parameters and the ratio of the electron-acceptor moiety in copolymer that is responsible for the density of electron donor–acceptor pairs. This correlation was discussed in terms of intermonomeric charge transfer interactions as intrinsic properties of materials, formed once with copolymer synthesis.

Methods

Experimental procedures

This study was performed on a series of statistical copolymers of two methacrylic monomers with electron-donor and electron-acceptor pendant groups, respectively. One monomer had *N*-ethyl-3-hydroxypropyl phenothiazinil methacrylate as electron-donor (D) pendant group on the methacrylic unit while the other one had the methacyloyl-*β*-hydroxyethyl-3,5-dinitrobenzoate as electron-acceptor (A) pendant group, as shown in Fig. 1. The composition of copolymers was expressed by the molar ratio of electron-acceptor/electron-donor (A/D) groups, as determined together with molecular weight by GPC measurements in DMF (calibrated with PS standard) and presented in Table 1.

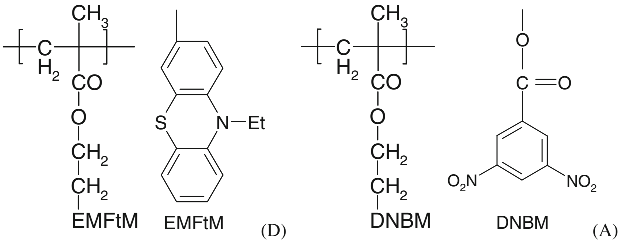

Fig. 1 Chemical structure of pendant electron-donor (D) and electron-acceptor (A) groups of the methylmethacrylate monomers

Formation of intramolecular (intermonomeric) electron transfers in these copolymers was proved by UV–VIS and ^{1}H-NMR at 60 MHz [47]. ^{1}H-NMR analysis at 400 MHz showed a statistical sequence of monomers distribution.

Calorimetric data were collected with Pyris Diamond DSC (Perkin Elmer) instrument used both in standard and in StepScan DSC mode of analysis. Sample weights were of about 8.5 mg and nitrogen was used as purged gas for an inert atmosphere and good thermal conductivity, at a flow rate of 20 mL min^{-1}. Firstly the samples were pretreated to erase thermal history and to allow a good formation of glassy state. The procedure consisted in heating by 10 °C min^{-1} from 30 °C up to 150 °C, maintaining for 1 min at 150 °C then slowly cooling back to 30 °C by 10 °C min^{-1}.

In standard mode DSC analysis samples were heating up by 10 °C min^{-1} up to 150 °C and scanned. The reproducibility of glass transition behavior for at least three runs showed that the intramolecular interactions between the electron-donor and the electron-acceptor pendant groups in our copolymer series are strong enough to not be affected by the increase of thermal energy when passing through the glass transition. The data collected was used to determine glass transition temperature (T_g) as mid-point of step in heat flow of sample. For standard mode DSC instrument was calibrated using Indium as standard for melting temperature and heat flow measurements.

The StepScan procedure used the following experimental parameters: in each cycle a linear heating rate of 10 °C min^{-1} for the dynamic segment increases the temperature with 2 °C (mean step amplitude) and an equilibrium criterion of 0.001 mW that automatically determined the length of the isothermal segment that followed each dynamic segment. The dynamic/isothermal heating cycles started at 30 °C and were repeated up to 150 °C. The data analysis software automatically separated the thermodynamic (reversible) and kinetic (irreversible) C_p data. Glass transition temperature was calculated as mid-point of step in heat capacity of sample in reversible signal (thermodynamic C_p). StepScan DSC minimized the systematic errors due to calibration for C_p measurements using sapphire (Al_2O_3).

Densities of samples were measured by pycnometry in methyl alcohol at 25 °C.

Table 1 Composition expressed as electron-acceptor/electron-donor (A/D) ratio and molecular mass of methylmethacrylate copolymer series

Characteristic	Sample code								
	D	P1	P2	P3	P4	P5	P6	P7	A
A/D ratio	0	0.10	0.22	0.35	0.53	0.60	0.72	0.76	1
Mw × 10^3/g mol^{-1}	138	104	83	79	72	78	64	67	67

Evaluation of CRR size and related parameters

Experimental parameters used for calculation of CRR size was extracted from the reversible signals from StepScan DSC experiments as described. The CRR size, the volume of CRR region ($V_\alpha = \xi_\alpha^3$) as well as the number of particles, considered in case of polymers as the monomeric units (N_α) in one average CRR volume were calculated according to Donth relationships [5]:

$$\xi_\alpha^3 = k_B T_g^2 \frac{\Delta\left(\frac{1}{C_v}\right)}{\rho(\delta T)^2} \tag{1}$$

$$N_\alpha = \frac{\rho N_A \xi_\alpha^3}{M_0} \tag{2}$$

were N_A is Avogadro number, δT is the mean temperature fluctuation over a CRR volume, T_g is glass transition temperature, k_B is Boltzmann constant, ρ is sample density, $1/C_v$ is reciprocal volume heat capacity at constant volume and M_0 is molar volume of each monomeric unit, considered as particle included in CRR volume.

Mean temperature fluctuation (δT) was calculated by "rule of thumb" [21]: $\delta T = \Delta T/2.5$ on heating. ΔT represents the temperature interval where $C_p(T)$ of sample varies between 16 and 84% from total ΔC_p step at glass transition. This important parameter was determined from the reversible signal in StepScan DSC in glass transition range as shown in Fig. 2.

Donth defined the step of reciprocal volume heat capacity in glass transition range as:

$$\Delta(1/C_v) = (1/C_v)^{\text{glass}} - (1/C_v)^{\text{liquid}} \tag{3}$$

were $(C_v)^{\text{glass}}$ and $(C_v)^{\text{liquid}}$ are the volume heat capacity in glass and liquid state, respectively.

Another way to calculate the reciprocal volume heat capacity was proposed by Hunth et al. [48] and used by other authors, as following:

$$\Delta\left(\frac{1}{C_p}\right) = \frac{\Delta C_p}{\left(\overline{c_p^{T_g}}\right)^2} \tag{4}$$

where $\overline{c_p^{T_g}} = ((C_p)^{\text{liquid}} + (C_p)^{\text{glass}})/2$ is the mean average heat capacity between glass and liquid state at the limits of glass transition range. This value was determined at glass transition temperature, as shown in Fig. 2.

For ξ_α calculation we considered the approximation of Hempel et.al. [21] that neglects the difference between the heat capacities at constant pressure and the heat capacities at constant volume. This allows to replace C_p with C_v, and therefore to calculate $(C_v)^{\text{glass}}$, $(C_v)^{\text{liquid}}$, and $\Delta(1/C_v)$ at T_g from the variation of C_p signal that is directly available through the StepScan experiments. By both Donth and Hunth methods were calculated values of $\Delta(1/C_p)$, and was observed some little differences, which showing same evolution function of electron-acceptor monomer ratio. Therefore, based on this will use values extracted from reversible signals of StepScan according only to Donth method for CRR size calculations.

Results and discussions

Heat flow variation with temperature as determined from standard DSC analysis of the copolymer series is presented in Fig. 3. All copolymers have glass transition temperatures higher than the corresponding homopolymers showing that the chain mobility was strongly reduced. On the other hand the range of glass transition was not visibly affected by the copolymer composition even the clearly T_g changed. This behavior is different to other polymer systems (e.g., crosslinked ones) that show a net broadening of glass transition range when the mobility is drastically reduced. It is clear that glass transition temperature depends on copolymer composition. T_g has maximal values

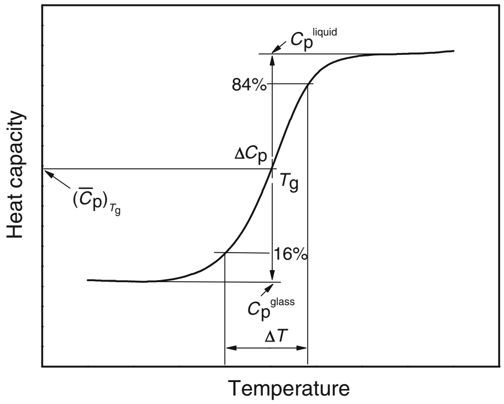

Fig. 2 Evaluation of ΔT and $\left(\overline{C_p}\right)_{T_g}$ from reversible StepScan DSC signal

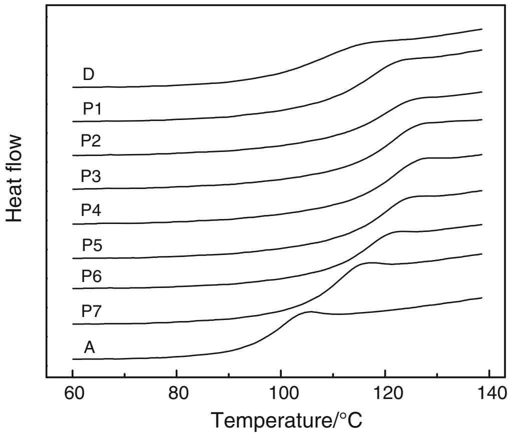

Fig. 3 Standard DSC signals for copolymer series

Table 2 Reciprocal heat capacity at constant presure and number of monomeric units in a CRR for methylmethacrylate copolymer series

Characteristic	Sample code								
	D	P1	P2	P3	P4	P5	P6	P7	A
$\Delta(1/C_p)$*/g °C J^{-1}	0.136	0.116	0.098	0.088	0.091	0.097	0.107	0.111	0.13
N_α	137	101	76	64	66	72	86	95	136

* Values for reciprocal heat capacity were calculated as described by Donth (see Fig. 2)

when electron-acceptor monomer moiety has values between 0.3 and 0.6 and decreases towards extreme compositions.

The electron transfers occur by pairs of electron-donor and electron-acceptor groups, their number depending on copolymer composition. Based on this we can say that glass transition temperature in our copolymer series has an evolution with the number of pairs of donor–acceptor electron that generates the intramolecular electron transfers. This explains the maximal values of T_g when the number of electron-donor groups is similar to that of electron-acceptor groups (balanced ratio of pendant groups) that gives maximal number of pairs.

Based on an early study [49], one can say that a weak charge transfer complexes appeared between electron-donor and electron-acceptor pendant groups by electron transfer process with effect in reducing the flexibility and mobility of polymer chains. It is clear that chemical structure of pendant groups has a major contribution on the charge transfer complex with an effect on reducing the chain mobility of copolymers.

Both intramolecular and intermolecular interactions could simultaneous act in a polymeric material, but their distribution in glassy state is irregular because limited mobility induces structural heterogeneity. Heating a polymer sample over its T_g increases structural homogeneity and decreases the density of intermolecular interactions because the mobility of chains allows the arrangement of macromolecules in a quasi-equilibrium state determined mainly by the intramolecular interactions. Slowly cooling through the glass transition range conserves the density of both intra- and inter-molecular interactions. Therefore, the effect of intermolecular interaction is minimized by the pretreatment procedures applied to our samples, as explained above. On the other hand the statistical distribution of electron-donor and electron-acceptor pendant groups on our macromolecular polymethacrylate chains favors the formation of intramolecular electron transfer interactions. Considering these aspects we could safely neglect in our study the intermolecular interactions and consider only the intramolecular ones. These are weak interactions, however, if their number is high enough their global effect can influence both the chain mobility and the cooperative region, as discussed below.

From reversible signals of StepScan DSC were determined the T_g, δT, and $\Delta(1/C_p)$ following the methods presented in experimental part, as these values are necessary to calculate the CRR size and related parameters. Values for $\Delta(1/C_p)$ are presented in Table 2, and T_g values extracted both from StepScan and form standard DSC are comparatively shown in Fig. 4 as function of electron-acceptor monomer ratio in our copolymer series. Is clear to observe that a similar evolution of T_g with copolymer composition was found by both methods. Moreover, the difference between the values measured by standard and StepScan DSC is of maximum 2 °C that is commonly accepted. Since StepScan DSC minimize the errors as mentioned in introduction part, we used the T_g values determined by this method for our calculations of CRR sizes, as well for number of monomeric units on CRR (N_α).

Calculated values for CRR sizes and CRR volume are presented in Fig. 5 function of copolymer composition. These values are in same range of 1–5 nm reported by other authors for various polymer systems. For example the CRR values found for poly(*n*-alkyl methacrylate)'s were around 1 nm and decreased as the number of C-atoms of *n*-alkyl side groups increased due to an internal plasticizing effect [5]. Higher CRR sizes of about 3.2–4 nm found for our methacrylate copolymer series could be explained by the presence of relative bulky side groups containing phenothiazinine and dinitrobenzoate units that increase the

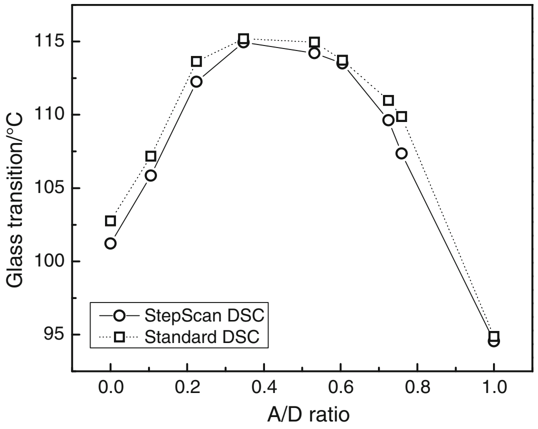

Fig. 4 Variation of T_g with electron-acceptor/donor ratio of pendant groups in copolymers as determined by standard and StepScan DSC

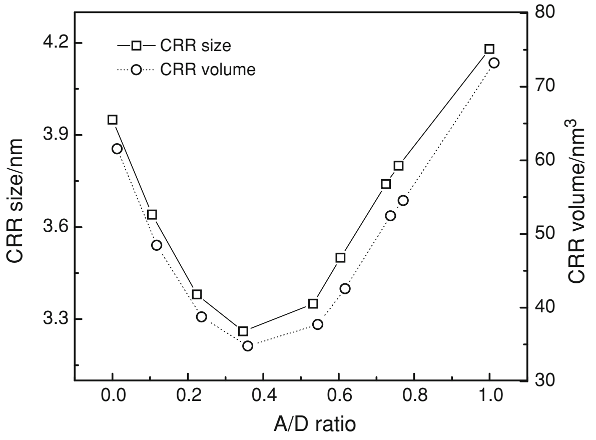

Fig. 5 Variation of CRR size and volume with electron-acceptor/donor ratio of pendant groups copolymers

free volume and therefore the number of conformational states of copolymer chains.

The values calculated for the CRR size of our copolymer series lays close to the uncertainty range of 9% that is usually accepted [21]. However, these small differences are caused mainly by the very weak interactions and interaction changes caused by the variation of electron-donor and electron-acceptor moieties in the structure of copolymers. The most important observation from Fig. 5 is the general trend of the CRR size in the series rather than its exact value. Minimal values for CRR sizes and CRR volume were observed for balanced composition in our copolymer series, which could be explained in terms of intramonomeric electron transfers between the electron-acceptor and the electron-donor containing groups. The rearranging processes in glass transition range are affected by the decreasing of cooperativity in copolymers. This could be explained by the fact that balanced composition of electron-donor and electron-acceptor groups allows maximal probability to form electron transfers interactions, that decreases the length scale motions associated with glass transition. Maximal densities of electron transfers reduce chain movements therefore less conformational states become available, inducing lower values for CRR sizes and volume. This is in good agreement with Sillescu that correlated the CRR size with the available conformational states [6]. Going to extreme composition of copolymers the CRR size and volume increase to maximal values corresponding to homopolymers. The number of monomeric units (N_α) inside CRR volume also has minimum values for balanced composition of copolymers as presented in Table 2.

Stronger intramolecular interactions due to more electron donor–acceptor pairs and minimal number of interacting units inside small CRR show a loss of cooperativity. Therefore, the rearranging processes involving global movements of structural units in glass transition range become more difficult to activate at balanced composition. This results in a shift of glass transition to higher temperatures as well as in an increase of mean thermal fluctuation. Indeed, δT calculated by StepScan DSC shows similar trend with copolymer composition as T_g does (Fig. 6a). On the other hand, stronger intramolecular interactions at balanced compositions of copolymers limits the number of conformational states even after the glass transition, thus decreasing the variation of C_p through the process (Fig. 6a). These observations show that the intramolecular interactions affect both the kinetic and thermodynamic behavior of the glass transition.

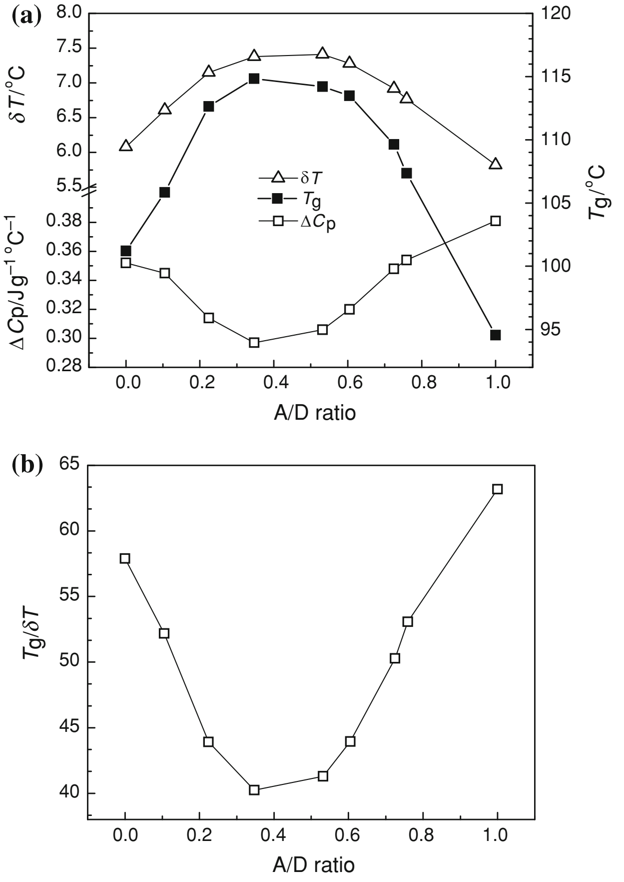

Fig. 6 Evolution of mean fluctuation temperature (δT), glass transition (T) and ΔC_p (**a**) and of $T_g/\delta T$ ratio (**b**) with electron-acceptor/donor ratio of pendant groups in methyl methacrylate copolymers

The most interesting observation is that even the T_g and the (δT) pass to maximum values, their ratio passes through minimum values (Fig. 6b). This suggests that the copolymer composition affects mainly the mean thermal fluctuation (δT) rather than the glass transition temperature. Therefore, the intramolecular electron transfer interactions in our copolymer series decrease the cooperativity while increasing the thermal fluctuations, the effect on the rearranging processes at glass transition being mainly kinetic.

Conclusions

A series of statistical methacrylate copolymers with intramolecular electron transfers between pendant electron-donor and electron-acceptor pendant groups was studied by StepScan DSC in order to determine the effect of copolymer composition on the parameters which describe the cooperative rearranging region. Minimal values for CRR size and CRR volume as well as for N_α were found at balanced composition of copolymers (0.4–0.6 ratio). T_g and mean fluctuation temperature (δT) had maximum values in this composition range.

A loss of cooperativity in rearranging processes in glass transition range was observed, similar to crosslinked polymer systems, polymer nanocomposites or other polymer systems confined in different nanostructures. This was explained for our copolymer series in terms of intramolecular electron transfers between the electron-donor and electron-acceptor groups. A decrease of $T_g/\delta T$ was observed suggesting that the effect of intramolecular interactions on the rearranging processes at glass transition is mainly kinetic.

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