Thermoreversible Crosslinking of Silicones Using Acceptor-Donor Interactions

Emmanuel Pouget, François Ganachaud, and Bernard Boutevin

Abstract Partial charge transfer between donor and acceptor groups has been used as a tool to physically structure silicone materials. In a first part, interactions between a single donor molecule, i.e. 9H-carbazole-9-ethanol, and a poly(dimethylsiloxane) functionalized on both chain-ends by acceptor groups, i.e. 3,5-dinitrobenzoate, were studied by DSC and UV-Vis analysis. The thermoreversibility of the interactions was likely demonstrated by UV-Vis analyses, which also showed a most favourable association of the complex for a 1/1 stoechiometry. The second part of this work deals with the synthesis of a triblock copolymer poly (2-(N-carbazolyl) ethyl methacrylate)-*b*-poly(dimethylsiloxane)-*b*-poly(2-(N-carbazolyl) ethyl methacrylate) by atom transfer radical polymerization in the presence of copper bromide and 1,1,4,7,10,10-hexamethyltriethylene tetramine in THF. The association of this triblock copolymer with the telechelic acceptor–based poly(dimethylsiloxane) used in the model study has been checked by rheology, which showed on heating and cooling a thermoreversible elastic/viscoelastic transition.

1 Introduction

Current silicone elastomers produced in the industry are made of long chemically crosslinked PDMS chains in which silica fillers are introduced to increase the mechanical properties of the material, thus preventing its recycling. Recently, Wacker Company commercialized a non-chemically crosslinked silicone elastomer

F. Ganachaud
Institut Charles Gerhardt – UMR 5253 CNRS, Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'école normale, 34296 Montpellier cedex 5, France
e-mail: ganachau@enscm.fr

called Geniomer®, [1–4] a multiblock copolymer made of urea-PDMS sequences. Supramolecular interactions [5–8] between urea or urethane groups, based on strong plural hydrogen bonding, has already been shown to structure silicones for quite a long time. For instance, Yilgor et al. and others [9–16] demonstrated that the strength of the hydrogen bonds had a direct influence on mechanical and thermal properties of the material, silicone-urethane systems being less efficient than silicone – urea systems. Also, the phase segregation between hard segments, namely crystalline urea or urethane, and soft poly(dimethylsiloxane) segments generates a thermoplastic elastomer, without the need of adding silica particles. Colombani et al. [17] studied slightly different supramolecular PDMS, introducing bisurethanes as side groups. They observed also a great improvement of mechanical properties, ascribed to an organization of the material as detected by Small Angle X-Ray diffraction. They also showed that, between 100 and 140°C, the material is easy to reprocess whereas at higher temperatures, degradation reactions produced isocyanate and amine groups back, which, by anarchic reactions, chemically crosslinked the material.

In this context, we ought to develop physically crosslinked silicone materials, starting from PDMS functionalized by carbazole (electron donor) and dinitrobenzene (electron acceptor) groups. The partial electron transfer between donor and acceptor groups has been reviewed by Simionescu et al. [18], and its application to the compatibilization and enhancement of mechanical properties of functionalized polymers described in several research articles [19–24]. Particularly, the glass transition temperature (T_g) and the temperature of decomplexation (T_m) were the highest while mixing a (poly(2-(3,5-dinitrobenzoyloxy)ethyl methacrylate) (acceptor polymer) and a (poly[2-(9-ethyl) carbazolyl methyl methacrylate]) (donor polymer) of low molar masses. [21] To our knowledge, only one report of Zentel et al. [25] studied some PDMS modified by acceptor/donor groups. A series of poly(dimethylsiloxane)s (PDMS) was functionalized either by electron donor (N-ethyl carbazole) or electron acceptor (3,5-dinitrobenzene) groups, statistically arranged along the polymer chain or grafted at the chain-ends (telechelic polymers). Blending of the donor- and acceptor-modified statistical copolymers led to a strong increase of the melt viscosity as a consequence of complex formation. In contrast to this, no significant enhancement of the viscosity was observed in blends of telechelic polymers, since only a linear chain extension was believed to occur in this case.

In this paper, we first present a model study on blending a α,ω-3,5-dinitrobenzoate PDMS and free 9H-carbazole-9-ethanol, in order to check whether the recently proposed 1:1 stoichiometry between carbazole and dinitrobenzoate molecules indeed applies (Scheme 1). [26] Then, we describe the preparation of triblock copolymers, poly[2-(N-carbazolyl)ethyl methacrylate]-*b*-PDMS-*b*-poly[2-(N-carbazolyl)ethyl methacrylate] (P(CzEMA)-*b*-PDMS-*b*-P(CzEMA)), using Atom Transfer Radical Polymerization (ATRP), and their blending with the acceptor-functionalized PDMS. In both studies, the physical association and thermal reversibility of these were followed by different techniques, including UV-Vis spectroscopy, DSC or Rheology.
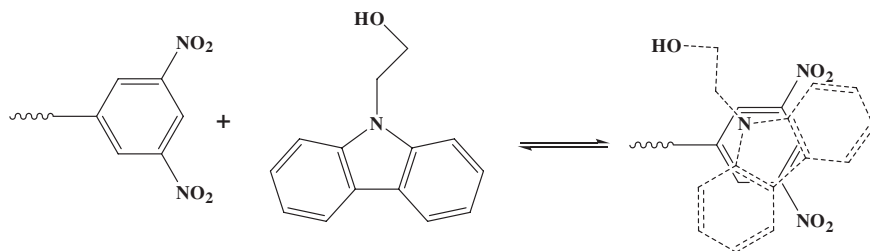
Scheme 1 Proposed geometry of the complex between a dinitrobenzoate and 9H-carbazole molecules, as given in ref. [26]

2 Experimental Part

Materials. The α,ω-(3-hydroxypropyl)polydimethylsiloxane was a gift of Rhodia Silicones. All other chemicals were purchased from Aldrich, unless stated. 3,5-dinitrobenzoyl chloride (98%), 9H-carbazole-9-ethanol (95%), dichloromethane (for analysis), octamethylcyclotetrasiloxane (D_4, Shin-Etsu, 99%), TONSIL EXE0096 (Süd-Chemie), 2-bromoisobutyryl bromide (98%), HMTETA (1,1,4,7,10,10-hexamethyltriethylene tetramine, 98%), copper bromide (98%) and triethylamine (98%) were used as received. Methacryloyl chloride (97%) was distilled before use. All reactions were carried out under inert nitrogen atmosphere.

Synthesis of the α,ω-(3,5-dinitrobenzoate)PDMS. Typically, 10 g of α,ω-(3-hydroxypropyl)polydimethylsiloxane ($M_{n,SEC} \approx 970\,g.mol^{-1}$, 10.3 mmol) were reacted with 5.229 g of 3,5-dinitrobenzoyl chloride ($M = 230.56\,g.mol^{-1}$, 22.6 mmol) in 50 mL dichloromethane at 0°C during 1 h and then at room temperature overnight. The solution of the 3,5-dinitrobenzoyl chloride was added dropwise onto the solution of the PDMS containing 2.29 g of triethylamine ($M = 101.19\,g.mol^{-1}$, 22.6 mmol) used to trap hydrochloric acid formed during the reaction. After filtration of the triethylammonium chloride, an extraction of the excess of 3,5-dinitrobenzoyl chloride by a basic aqueous solution was carried out. After drying over $MgSO_4$, the product was recovered by removal of dichloromethane under vacuum. The reaction is quantitative (>98%).

Synthesis of the α,ω-bromoPDMS macroinitiator. Typically, 10 g of α,ω-(3-hydroxypropyl)polydimethylsiloxane ($M_{n,SEC} \approx 970\,g.mol^{-1}$, 10.3 mmol) were reacted with 5.21 g of 2-bromoisobutyryl bromide ($M = 229.9\,g.mol^{-1}$, 22.6 mmol) in the presence of 2.29 g of triethylamine ($M = 101.19\,g.mol^{-1}$, 22.6 mmol) in 50 mL dichloromethane at 0°C during 3 h and then at room temperature overnight. The 2-bromoisobutyryl bromide was added drop-by-drop onto the solution of triethylamine and PDMS. After filtration of the triethylammonium bromide salt formed during the reaction, a basic extraction

was carried out to remove the excess of 2-bromoisobutyryl bromide. After drying, the pure di-bromo telechelic PDMS macroinitiator was recovered by removal of dichloromethane under vacuum.

Redistribution of the PDMS macroinitiator with octamethylcyclotetrasiloxane (D$_4$). This reaction allowed to increase the molecular weight of the PDMS macroinitiator. Typically, the PDMS macroinitiator synthesized during the previous step ($M_n = 1270$ g.mol^{-1}, 1.6 g, 1.26 mmol) was introduced in a round-bottom flask equipped with a magnetic stirrer. 23 g of D$_4$ ($M = 296.6$ g.mol^{-1}, 77 mmol) and 0.23 g of TONSIL (a sulfonic acid modified clay) were added to the flask. The solution was stirred and heated at 80°C during 72 h. A pure product was recovered by filtration of the catalyst and precipitation of the polymer in excess methanol. Results: $M_{n,th} = 19400$ g.mol^{-1}, $M_{n,RMN} = 21100$ g.mol^{-1}, $M_{n,SEC} = 20900$ g.mol^{-1}, PDI = 1.49, yield: 85%.

Synthesis of 2-(N-carbazolyl)ethyl methacrylate. 9H-carbazole-9-ethanol ($M = 211.3$ g.mol^{-1}, 10 g, 47.3 mmol) was added dropwise to a solution of freshly distilled methacryloyl chloride ($M = 104.5$ g.mol^{-1}, 14.8 g, 141.2 mmol) and triethylamine ($M = 101.19$ g.mol^{-1}, 5.05 g, 50 mmol) in 100 mL dichloromethane at 0°C during 1 h. Then the solution was stirred overnight at room temperature. After filtration, the solution was extracted with a slightly basic aqueous solution to remove the excess of methacryloyl chloride. After drying over MgSO$_4$, the pure product was recovered by removal of dichloromethane under vacuum at room temperature (yield: 60%).

Atom Transfer Radical Polymerization of 2-(N-carbazolyl)ethyl methacrylate. The conditions of polymerization were adapted from the study published by Zeng et al. [27] The ATRP of CzEMA (277 g.mol^{-1}, 0.3437 g, 1.24 mmol) was carried out at 60°C under argon atmosphere in THF, in the presence of copper bromide (142.7 g.mol^{-1}, 13.7 mg, 96 µmol) and HMTETA (229.2 g.mol^{-1}, 22 mg, 96 µmol). The solution of the PDMS macroinitiator (Mn = 20900 g.mol^{-1}, 1 g, 4.79 10^{-5} mol) dissolved in 1 mL of THF was bubbled under argon during 15 min, and then introduced in the round-bottom flask containing the solution of CuBr, HMTETA and CzEMA in 3 mL THF, previously freeze-thawed three times. After 7 h at 60°C, the monomer conversion was quantitative. The polymer was precipitated in methanol, filtrated, dissolved in a little amount of THF and passed through a silica column to remove the copper species. THF was then removed under vacuum before characterization.

Characterizations. Size Exclusion Chromatography (SEC) apparatus was composed of a SpectroSeries P100 pump equipped with a Shodex Rise-61 refractometer detector and two 300 mm columns thermostated at 30°C (mixed-D PL-gel 5µm columns from Polymer Laboratories: $2 \times 10^2 - 4 \times 10^5$ g.mol^{-1} molecular weight range). Toluene was used as the eluent at a flow rate of 0.8 mL.min^{-1}. Calibration was performed with polystyrene standards from Polymer Laboratories. ^{1}H NMR analyses were performed in CDCl$_3$ on a Bruker Advance 250 MHz. UV-Vis analyses were performed on a spectrometer UV-Vis mono-beam HP8453. Rheology experiments were carried out on a TA instruments AR1000 apparatus between 15°C and 205°C. Every 10°C, after 1 minute of equilibration, 10 measurements were made

between 1 and 10 rad.s^{-1}. The experiment was carried out on heating and cooling. We chose 25°C as the temperature of reference for building temperature/frequency master curves.

3 Results and Discussion

3.1 Model Study

This study has been carried out to analyze the nature of the complex formation between 9H-carbazole-9-ethanol and dinitrobenzoate groups attached at each chain-ends of a short PDMS backbone. The polymer was prepared in very good yields (>98%) by esterification of 3,5-dinitrobenzoyl chloride and α,ω-(3-hydroxypropyl) PDMS. ^{1}H NMR (Fig. 1) confirmed that the reaction was quantitative. The protons of the methylene group located near the hydroxyl group totally disappeared after functionalization. On the contrary, the signal of the protons of the methylene situated in α position of the ester appeared at 4.3 ppm. The signals of the aromatic protons also showed up on the final product at 8.8–9 ppm.
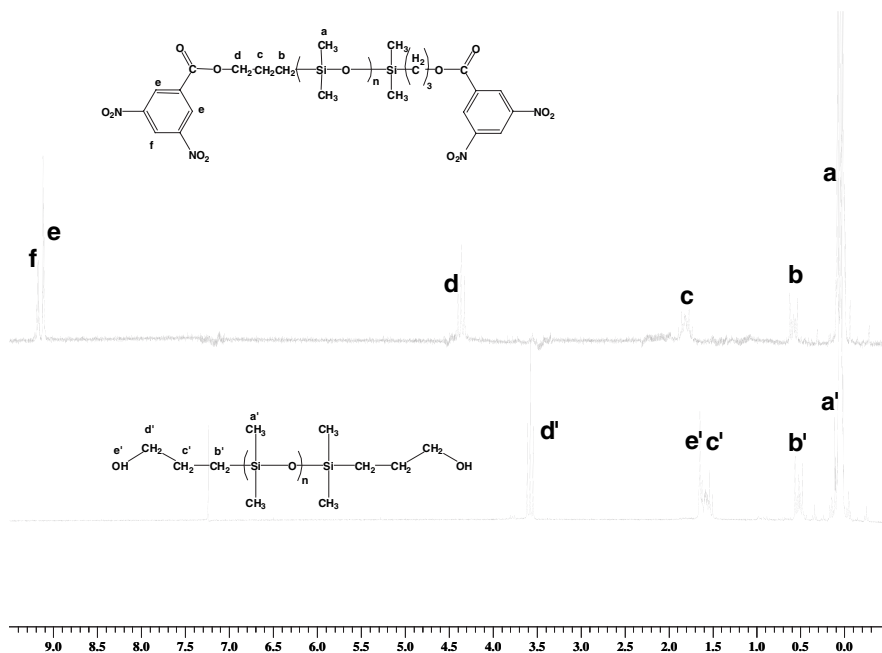

Fig. 1 ^{1}H NMR of hydroxy-functionalized PDMS (*bottom*) and α,ω-(3,5-dinitrobenzoate) PDMS (*top*)
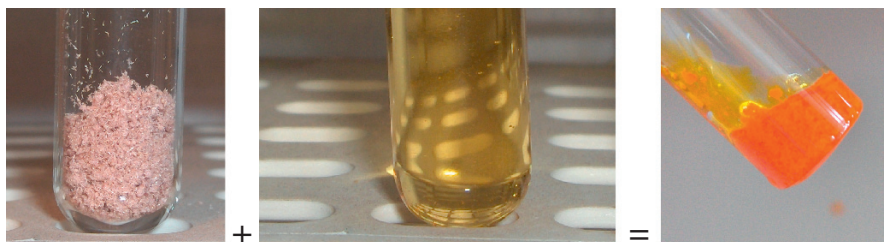
Fig. 2 9H-carbazole-9-ethanol powder (*left*), oily α,ω-3,5-dinitrobenzoate PDMS (*center*) and final melted-like strong orange complex of both species (*right*) (See also Plate 14 in the Colour Plate Section)

Both 9H-carbazole-9-ethanol and α,ω-dinitrobenzoate PDMS were mixed in stoichiometric conditions ([acceptor] = [donor] = 0.4 mol.L^{-1}) in dichloromethane at room temperature, giving instantaneously a strong orange solution, showing that acceptor and donor groups were instantaneously associated. Then dichloromethane was removed at room temperature during 72h to give viscous oil with a strong orange tint (Fig. 2).

We studied the thermoreversibility of the complex by DSC (Fig. 3). When heating, an endothermic phenomenon corresponding to the decomplexation between acceptor and donor groups was observed at 18°C. When cooling the material, an exothermic formation of the complex was detected at −10°C. During the second heating, the decomplexation of the complex was again picked at 18°C, demonstrating the total thermoreversibility of the association between acceptor and donor groups. Such effect was confirmed by observations made by eyes: at room temperature, the material was very fluid whereas below 18°C, the material increased in viscosity.
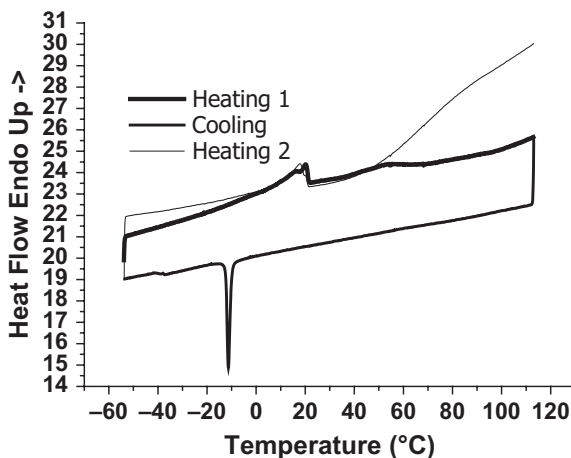

Fig. 3 DSC of the material formed by the association of free 9H-carbazole-9-ethanol and α,ω-(3,5-dinitrobenzoate) PDMS

To evaluate the best ratio between acceptor and donor groups, we carried out a UV-Vis analysis of chloroform solutions of the complex, with a concentration of donor and/or acceptor groups of 0.05 N. The spectra of the two primary products and of the charge transfer complex are presented on Fig. 4.

The Job's method [18, 26] consists in plotting, for different wavelengths, the values of UV absorbance at various acceptor/donor molar fractions, while keeping constant the total molar concentration of the solution [donor] + [acceptor] (here 0.05 N). The molar fraction ratio at the maximum absorbance point corresponds to the stoichiometry of the charge transfer complex. Figure 5 shows the Job plot for charge transfer complexation between α,ω-(3,5-dinitrobenzoate) PDMS and free 9H-carbazole-9-ethanol. The curves in Fig. 5 exhibit a maximum when the donor and the acceptor are in equimolar ratio, suggesting the formation of a 1:1 mole/mole complex, thus confirming the assumption made previously. [26] However, the fact that Job's curves are not symmetrical also prove that a larger complex is able to
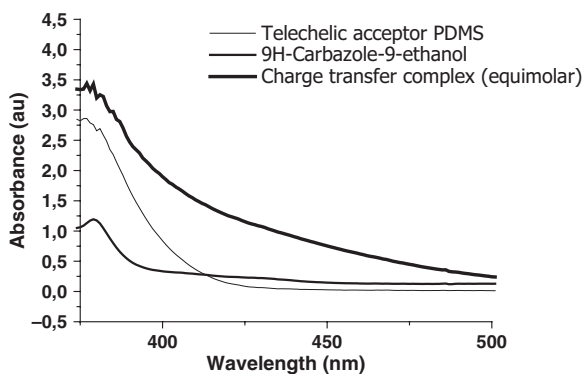
Fig. 4 CUV-vis spectra of 9H-carbazole-9-ethanol, α,ω-(3,5-dinitrobenzoate) PDMS and charge transfer complex in stoechiometric conditions
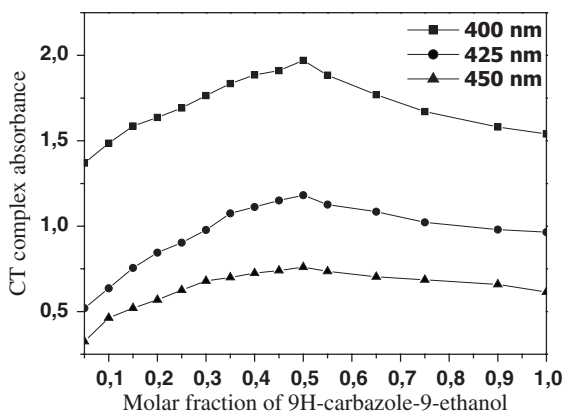
Fig. 5 UV-Vis Job plot for chloroform solutions of α,ω-(3,5-dinitrobenzoate) PDMS/9H-carbazole-9-ethanol between 400 and 450 nm

form in solution, thus explaining the viscosification of the charge transfer complex while removing the solvent.

3.2 *PCzEMA-b-PDMS-b-PCzEMA Triblock Copolymer Synthesis and Complexation with Dinitrobenzoate PDMS*

The monomer 2-(N-carbazolyl)ethyl methacrylate (CzEMA) was first prepared by reacting 9H-carbazole-9-ethanol with methacryloyl chloride, using an excess of triethylamine, in dichloromethane at 0°C. The yields of reaction were not very high (typically 60%) due to the presence of the nitrogen atom on the monomer, which can trap a proton during the reaction. This protonated monomer is eliminated while making several aqueous washes to remove the excess of salts in the product. The purity of the final monomer was demonstrated by ^{1}H-NMR (Fig. 6).

Besides, a di-bromo PDMS macroinitiator was prepared according to two reaction steps given in Scheme 2: first, an esterification of a α,ω-(3-hydroxypropyl) PDMS by bromoisobutyril bromide in dichloromethane in the presence of triethyl-amine (yields > 99%); second, a redistribution of this macroinitiator in the presence of D_4 and a strong acid resin catalyst to increase the average molar mass of the
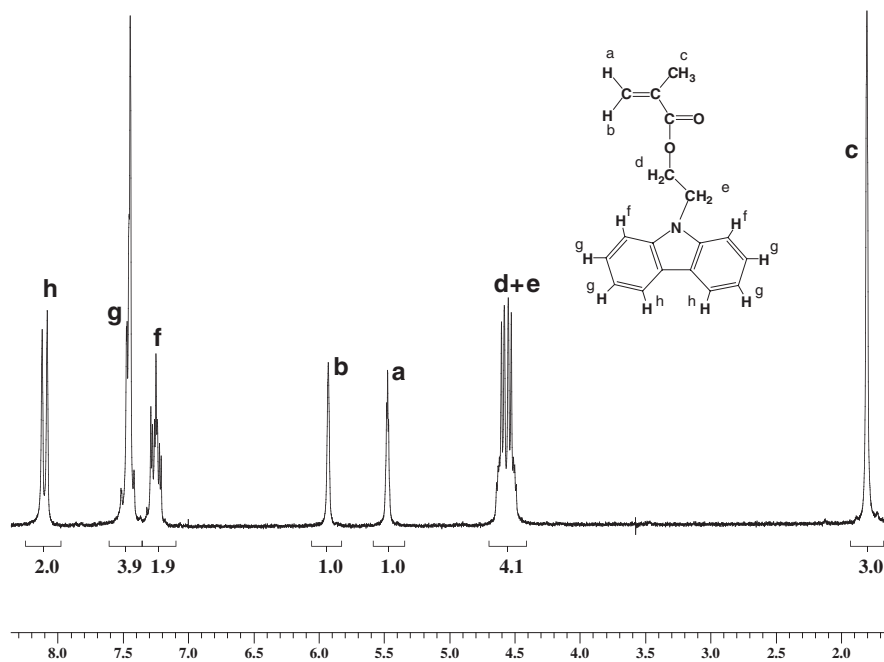

Fig. 6 ^{1}H-NMR of 2-(N-carbazolyl)ethyl methacrylate

Scheme 2 General scheme for the synthesis of the PCzEMA-b-PDMS-b-PCzEMA triblock copolymer. HMTETA is 1,1,4,7,10,10-hexamethyltriethylene tetramine

functionalized PDMS. After removal of the catalyst by filtration of the excess of D_4 by precipitation of the polymer, this latter has been analyzed by ^{1}H-NMR (Fig. 7) and size exclusion chromatography. The molecular weights obtained by NMR ($M_{n,NMR} = 21100$ g.mol^{-1}) and size exclusion chromatography ($M_{n,SEC} = 20900$ g.mol^{-1}) were found very close, which confirmed that the functionality of the polymer is retained during the redistribution reaction. Note that the macroinitiator could not be prepared the other way round, since the functionalization of long PDMS chains is unlikely.

The polymerization of CzEMA by ATRP, starting from the PDMS macroinitiator, was adapted from the protocol described by Zeng et al. [27] applied to the ATRP of 2-(dimethylamino)ethyl methacrylate, which has a structure quite similar to the CzEMA, i.e. in THF at 60°C using HMTETA and CuBr. The desired triblock copolymer PCzEMA-*b*-PDMS-*b*-PCzEMA was obtained in very good yields (monomer conversion >99%), and the final product analyzed by SEC (not shown) and ^{1}H-NMR (Fig. 8).

By SEC, we observed that the full distribution of PDMS chains shifted to large molar masses, thus proving the good initiation efficiency of such macroinitator. The final polydispersity index ($M_w/M_n = 1.25$) is smaller than the polydispersity index of the PDMS macroinitiator (1.49), another evidence that all PDMS chains were functionalized. The final molecular weight obtained by SEC for the triblock copolymer
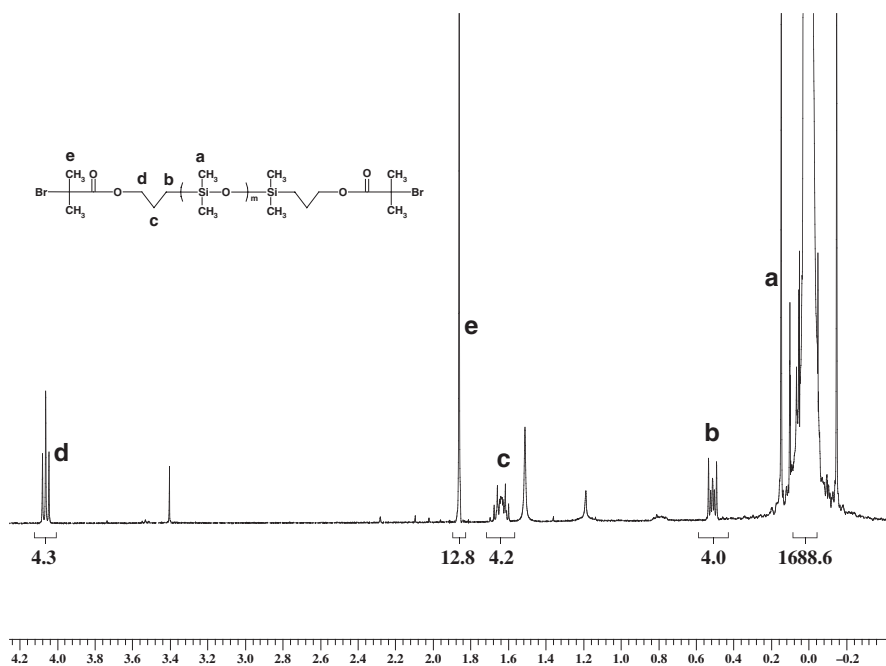

Fig. 7 ^{1}H-NMR of the di-bromo PDMS macroinitiator for the ATRP of CzEMA
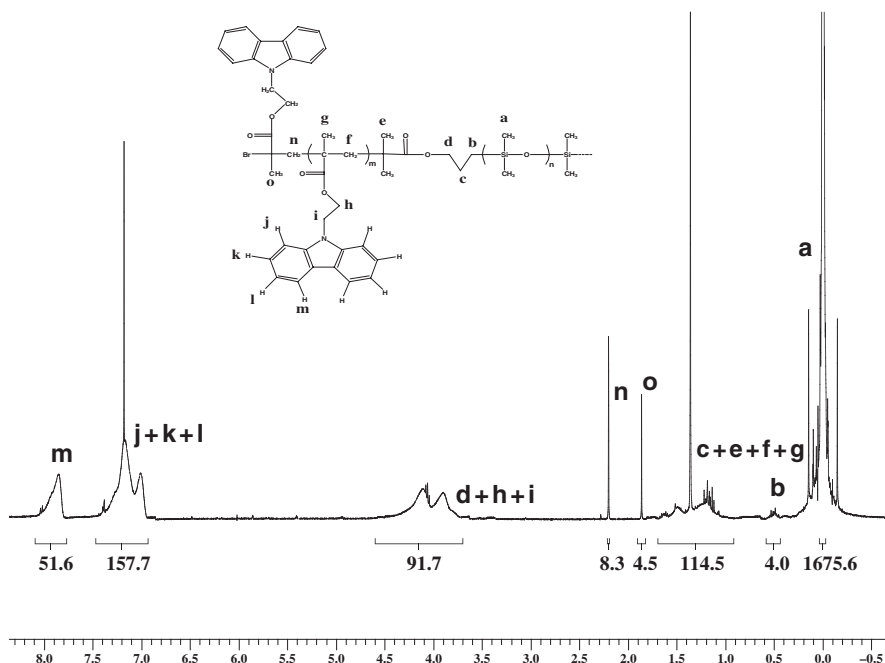
Fig. 8 ^{1}H-NMR of the PCzEMA-*b*-PDMS-*b*-PCzEMA triblock copolymer

($M_{n,SEC} = 31000\,g.mol^{-1}$) was higher than the theoretical molecular weight at the conversion ($28000\,g.mol^{-1}$ at 99%), since molecular weights were calculated on a polystyrene standard calibration.

This triblock copolymer was associated in dichloromethane, with the α,ω-(3,5-dinitrobenzoate) PDMS used in the model study, at a ratio between acceptor and donor groups strictly equal to 1. After solvent removal, a soft and lightly sticky material was obtained, again with a bright orange colour. No demixions were observed even after several cycles of heating and cooling. Since the DSC did not detect any complexation transitions, we directed our interests towards rheological experiments to unravel the thermal properties of our materials. The complex was submitted to one heating step and one cooling step cycle between 25 and 220°C, and measurements at different frequencies produced the master curves presented in Fig. 9.

Three domains were observed on these master curves, which overlapped perfectly for heating and cooling cycles. On heating, the material is viscous at high temperatures (>105°C). Between 105°C and 45°C, the material is elastic whereas under 45°C, the material is glassy. Such behaviour is typical of a thermoplastic elastomer, where here the transformation from an elastic solid to a viscous liquid is due to the decomplexation between acceptor and donor groups. Since a small number of interactions are exerted between acceptor and donor groups, the elastic domain is not very wide; besides, the glass transition zone is very low (<45°C) due to the presence of short PDMS chains acting as plasticizing agents. The fact that the viscous modulus G'' did
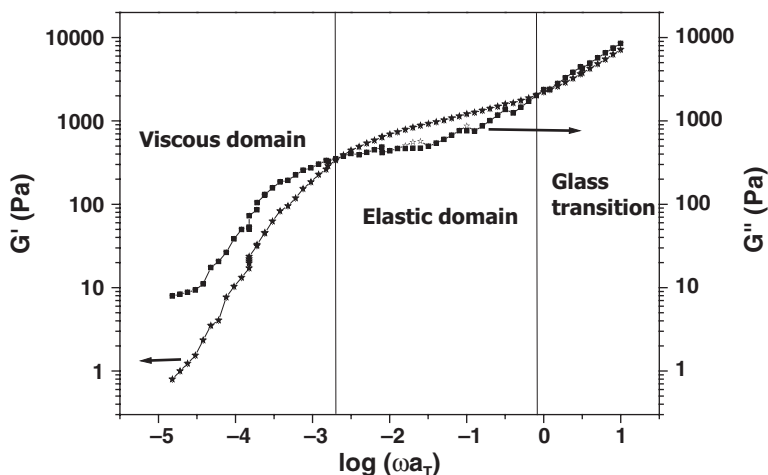
Fig. 9 Master curves obtained while heating (empty symbols) and cooling (full symbols) the material created by the association of α,ω-3,5-dinitrobenzoate PDMS with the PCzEMA-*b*-PDMS-*b*-PCzEMA triblock copolymer. Reference temperature: 25°C, (■) elastic modulus G', (*) viscous modulus G''

not show a minimum let one think that the elasticity of the material is due to the organization, rather than the entanglement, of the supramolecular chains. On cooling, the characteristic temperatures of the domains were found slightly different, as generally observed in DSC: the elastic domain is present between 95 and 30°C. This behaviour was reproducible upon heating and cooling few times, although some degradation reactions tended to occur at higher temperatures.

4 Conclusion

In conclusion, this study showed the possibility to thermoreversibly crosslink silicone elastomers using acceptor – donor interactions. The interactions are highly cooperative since a donor solid organic molecule, i.e. 9H-carbazole-9-ethanol, and a PDMS containing acceptor groups (3,5-dinitrobenzoyl groups) at the chain-ends are perfectly mixed together. A blend between this modified PDMS and a PCzEMA-*b*-PDMS-*b*-PCzEMA triblock was found stable on heating and cooling. The thermoreversibility of the interactions has been proved by rheological analysis. The preparation of blends between the triblock copolymer prepared in this study and PDMS containing many acceptor groups would be a solution to enlarge the elastic domain.

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