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Donor-Acceptor Complexation in Macromolecular Systems

1. Viscoelastic Properties of Poly-Donor – Poly-Acceptor Blends and of Corresponding Copolymers

H.A. Schneider, H.-J. Cantow, and V. Percec*

Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus,
Stefan-Meier-Straße 31, D-7800 Freiburg i.Br., Federal Republic of Germany

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SUMMARY

Blends of donor-macromolecules - poly(N-(2-hydroxyethyl)-carbazolyl)methacrylate - with acceptor-macromolecules - poly(methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate) - exhibit unique dynamic mechanical properties over a broad range of frequency and temperature when compared with those of the components. The complexation between the unlike polymers determines the topology of the thermoreversible network. Plateau modulus is extended into the low frequency and high temperature region dramatically. Corresponding copolymers show up minor improvement of the properties only depending on the donor-acceptor ratio within the macromolecular chain. Thus, the efficacy of intermolecular thermoreversible crosslinking clearly is evidenced.

INTRODUCTION

In a series of papers the one of us $^{1-3}$ has described polymerization and copolymerization of a new acceptor monomer - methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate (DNBM) - and the donor monomer - N-(2-hydroxyethyl)carbazolyl methacrylate (HECM) -. The copolymerization turned out to be azeotropic type.

Up to now only few investigations on the mechanical properties of blends of donor and of acceptor polymers - tensile modulus and yield stress - have been performed by SULZBERG and COTTER ^{4} and OHNO and KUMANOTANI ^{5}. It seemed to be worthwile, consequently, to study the dynamic mechanical properties of the new polymeric donor-acceptor system over a broad temperature and frequency range. It was the aim of this work to compare the efficacy of intermolecular specific contacts between macromolecules with that of intramolecular contacts by comparring the properties of polyblends and of copolymers.

EXPERIMENTAL

Poly(HECM), Poly(DNBM) and three copolymers with 3/1, 1/1 and 1/3 donor (HECM) to acceptor (DNMB) ratio were employed. The molecular weights have been estimated by gel permeation chromatography in N,N'-dimethyl acetamide, with relative calibration with narrow molecular weight distribution polystyrenes. T_g measurements were executed on a PERKIN ELMER DSC-2, using heating rates from 2.5 to 20° C/min. The data were extrapolated to zero heating rate.

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* Permanent adress: Dept. of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA

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Viscoelastic measurements were performed with an INSTRON model 3250 Rotary Rheometer using the orthogonal mode - excentric rotating disks -. The measurements were executed within a 50^{o} temperature range around T_g + 90 K for each sample.

A 1/1 blend of poly(HECM) and poly(DNBM) was prepared by mixing the two homopolymer solutions (THF). The precipitated reddish polymer charge transfer complex was redissolved in DMSO at 150^{o} C. After evaporation of the solvent the sample was dried in vacuo to remove the residual solvent.

RESULTS AND DISCUSSION

Table 1: Molecular weights and T_g's

Polymer	molar ratio	M_w	T_g/K
Poly(HECM)		57000	415.9
Poly(DNBM)		12000	359.7
Copolymer (HECM/DNBM)	3/1	32000	414.3
	1/1	16000	403.9
	1/3	13000	389.6

Molecular weights and T_g's extrapolated to zero heating rate are presented in Table 1.

Figure 1 shows the DSC runs of these samples and of the polyblend prepared as described. The glass transition temperature of the latter could not be realized because an exothermic degradation started around 400 K. Additionally a 1/1 mixture of the homopolymers in melt is shown in the Figure. It is evident that complexation is not effective due to kinetic restrictions probably in the melt mixture. Apparently precipitation from solution only enables sufficient contact probability. The melt mixture shows up two T_g's at 359 and 413 K.

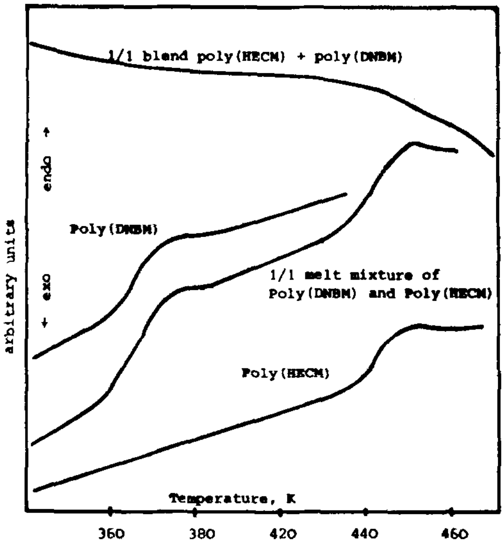

Figure 1: DSC curves of donor and of acceptor polymers and of 1/1 blend and melt mixture (10^{o}/min heating rate)

Although OHNO and KUMANOTANI [5] have evidenced a two phase structure of their blends, this could not verified for poly(HECM)-poly(DNBM) blends up to now. X-ray low angle measurements are in progress for this purpose.

In Figures 2 and 3 the mastercurves are presented for the storage modulus as well as for the dynamic viscosity. Moduli and viscosities have been normalized with respect to the T_g. For the blend the T_g of the corresponding 1/1 copolymer has been applied. For clarity of representation the moduli of the blend have been shifted o.5 log units upward in the ordinate.

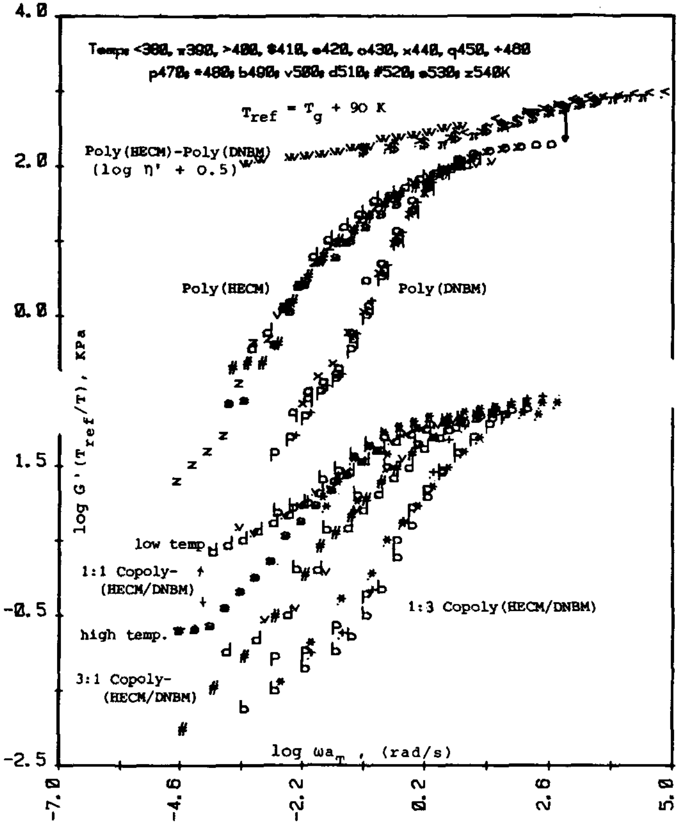

Figure 2: Storage moduli of the studied homo- and copolymers and of the 1/1 homopolymer blend. Ordinate shifted as described in the text and as indicated by the arrows.

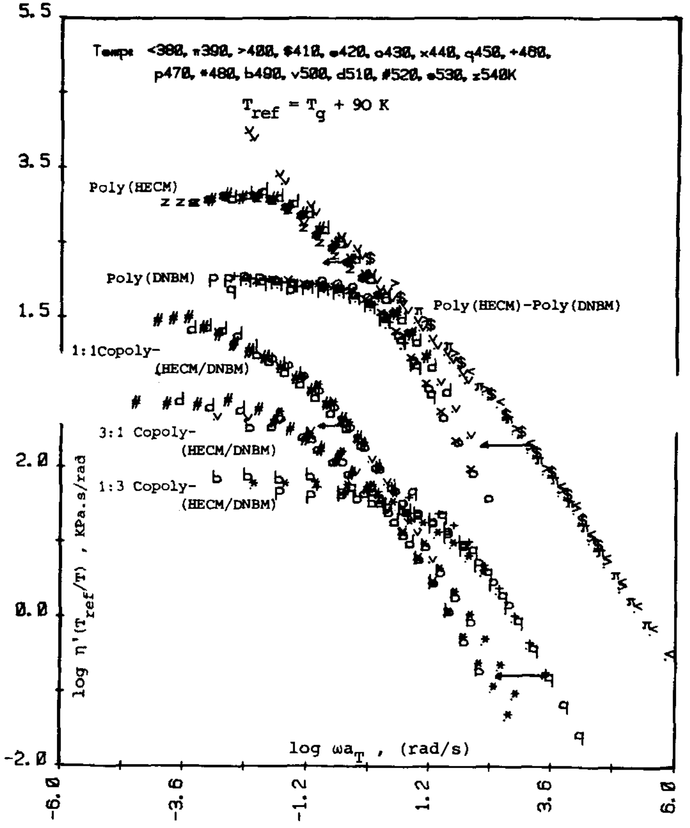

Figure 3: Dynamic viscosities of the studied homo- and copolymers and of the 1/1 homopolymer blend. Ordinate and abscissa shifted as described in the text and as indicated.

Correspondingly, the copolymer data have been shifted downward as indicated in the ordinate. Analogously, the dynamic viscosities were puzzled: Upper indication in the ordinate is valid for the homopolymers and for the blend. Additionally, data were shifted in the abscissa: + 0.5 for poly(HECM) and for 1/1 copoly(HECM/DNBM) and + 1.0 for the blend and for 1/3 copoly(HECM/DNBM).

It may be noted, first, that all samples reach the same plateau modulus approximatively, irrespective molecular weight and degree of complexation. Apparently, donor-acceptor contacts have no significant influence here. At lower frequencies and higher temperatures, however, the influence of intermolecular complexation is dramatic: The modulus of the blend built up by the complexing donor and acceptor macromolecules, respectively, reaches up to more than three orders of magnitude higher values than that of the homopolymers. In contrast, the copolymers exhibit temperature and frequency trend similar to that of the homopolymers, more pronounced for the 1/3 and for the 3/1 than for the 1/1 copolymer: Apparently, there is a limited chance in the equimolar copolymer for inter molecular charge transfer contacts. It clearly can be concluded from the elastic moddulus mastercurves that the inter molecular complexation produces a thermoreversible network with a specific topology, which extends the elastic region of the macromolecular system drastically.

The peculiar behaviour of the blend is also confirmed by the dynamic viscosity data. Newtonian behaviour is not reached within the measurable range. For the homo- and for the copolymer samples the value of the zero shear viscosity may be discussed in terms of molecular weight and of primary structure. The zero shear values of the 1/3 and of the 3/1 copolymers, respectively, are arranged according to the molecular weight of the samples. The 1/1 copolymer, however, demonstrates higher probability of donor-acceptor contacts by the fact that its zero shear viscosity is essentially higher than that of the 3/1 copolymer, irrespective the fact that the latter exhibit twice the molecular weight of the former.

In conclusion donor-acceptor complexation in macromolecular systems may offer interesting chances in realizing unique mechanical properties within a broad range of temperatures and frequencies. Inter molecular contacts apparently exhibit superior efficacy with respect to dynamic-mechanical properties when compared with intra molecular ones. Clustering of contact areas may be minimized in this way. Optimization of the macromolecular architecture of such systems is a challenge for preparative as well as for characterization work. One of the problems may be the minimization of the number of interacting groups within the macromolecular backbone with respect to the desired mechanical properties. An exciting approach is the idea to overpower the phase separation tendencies of unlike polymers by inserting interacting groups into the polymer backbones. Interesting thermodynamical aspects are connected with the problems discussed.

In following papers studies will be reported concerning minimization of the number of specifically interacting groups as well as concerning compatibilization of unlike macromolecules by complexation.

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