Polymer Bulletin 7, 263-270 (1982)

Polymer Bulletin

Donor-Acceptor Complexation in Macromolecular Systems

2. Synthesis and Viscoelastic Properties of Donor-Acceptor Complexed Poly(Methylmethacrylate)S and Poly(Buthylmethacrylate)S

H.A. Schneider, H.-J. Cantow, U. Maßen and H. Northfleet-Neto

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

SUMMARY

Copolymers of methyl methacrylate and of butyl methacrylate with N-(2-hydroxyethyl)carbazolyl methacrylate and with methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate, respectively, as charge transfer complexing agents have been prepared. Despite the low portion of the complexing components (1 and 10 mol %) the blends exhibit high level dynamic mechanical properties over an extended temperature and frequency range when compared with the unmodified homopolymers, poly(methyl methacrylate)s and poly(butyl methacrylate)s. The plateau modulus is extended into the low frequency and high temperature region to an extent comparable with that of blends consisting of donor and of acceptor subunits exclusively. The thermal stability is increased clearly.

The principle of intermolecular donor-acceptor complexation with the aim to optimize processibility as well as applicational properties may be conferred upon plastic and rubbery macromolecular systems with other types of backbones.

INTRODUCTION

In a series of papers PERCEC et al.[1)] have 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). In the first paper of this series SCHNEIDER, CANTOW and PERCEC [2)] have demonstrated that blends of poly(DNBM) and poly(HECM) show up interesting applicational properties caused by an intermolecular thermoreversible crosslinking effect due to the charge transfer interaction of the donor and acceptor groups. The thermal stability of the blends is limited, however.

0170-0839/82/0007/0263/$ 01.60

On the other hand this macromolecular system contains much more groups capable to interact than the maximum amount which may be effective within macromolecular chains.

EXPERIMENTS AND DISCUSSION

Consequently, donor-acceptor complexed polymethylmethacrylates were synthesized by radical copolymerization of methylmethacrylate with DNBM and HECM, respectively, at 60° C in dioxane, total amount of monomers .5 mol l^{-1}, using AIBN as initiator. In order to study the influence of longer side groups, butyl methacrylate was used as polymer backbone besides methyl methacrylate.

Copolymers obtained were characterized by elemental analysis and by NMR spectroscopy. Molecular weights were estimated by gel permeation chromatography in chloroform, with relative calibration with narrow molecular weight distribution polystyrenes. T_g measurements were executed with a PERKIN ELMER DSC-2, using heating rates from 2.5 to 20° C min^{-1}. Data were extrapolated to zero heating rate. Viscoelastic measurements were performed using the INSTRON 3250 Rotary Rheometer in the excentric rotating disks mode.

Table I presents the molecular weights, the extrapolated T_g's and the constants of the WLF equation of the studied polymeric systems.

Table I: Data of copolymers HECM and DNBM with MMA and BuMA and of polyblends. ($^+$ experimental, $^{++}$ iteration comp.)

	Polymer	$M_w \cdot 10^{-3}$	T_g/K	C_1^{+}	C_2	C_1^{++}
	PMMA	45.5	386.8	9.34	145.7	9.27
1	Copoly(.10HECM-.90MMA)	40.0	395.5	11.72	204.5	11.84
2	Copoly(.10DNBM-.90MMA)	44.0	388.4	11.31	174.0	11.20
3	Copoly(.10HECM-.90BuMA)	53.0	297.4	11.97	200.3	11.83
4	Copoly(.01HECM-.99BuMA)	49.0				
5	Copoly(.10DNBM-.90BuMA)	47.0	291.1	9.51	144.3	9.61
	1:1 w/w blend of 1 + 2		389.4	13.05	252.5	13.15
	1:1 w/w blend of 3 + 5		298.1	10.49	194.3	10.19
	1:1 w/w blend of 4 + 5		283.8	11.33	189.8	11.25

The experimental shift factors were linearized according to the WLF equation, FERRY [3], the obtained C_1 and C_2 constants being checked by the procedure described by MILLER [4]. Master curves were constructed with T_g + 90 K as the reference temperature.

The monophasic character of the blends was confirmed by their single T_g and by LAXR measurements.

In Figure 1 the master curves of the storage modulus of copolymer .10HECM -.90MMA is plotted by two ways, first,using the experimental a_T values and, second, using a_T's computed by iteration. Despite the fact that the latter values cause increased scatter of the data, this treatment of data appears to be the more consequent one.

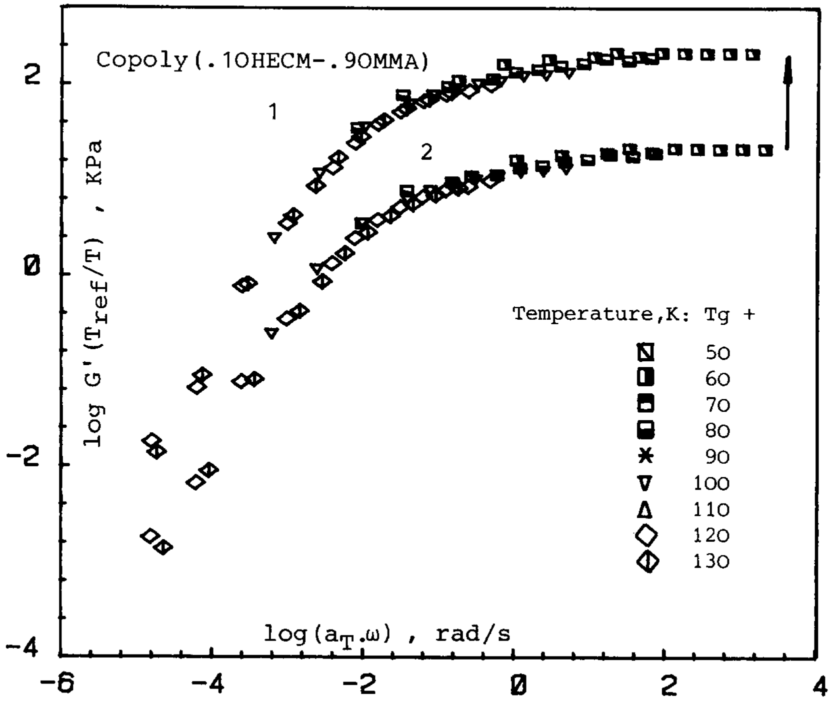

Figure 1: Master curves of the storage modulus
of Copoly(.10HECM-.90MMA)
1. using experimental a_T VALUES
2. using a_T's computed by iteration
(curve shifted by -1 along the ordinate

Figure 2 compares frequency and temperature dependence of this donor containing sample with that of PMMA homopolymer. Both polymers exhibit similar molecular weight. Even if the difference between the curves is not dramatical, the donor containing polymer shows up slightly increased plateau modulus, which may be caused by donor-donor interactions. At low frequencies and high temperatures, however, the MMA-HECM copolymer modulus drops sharper than that of the PMMA.

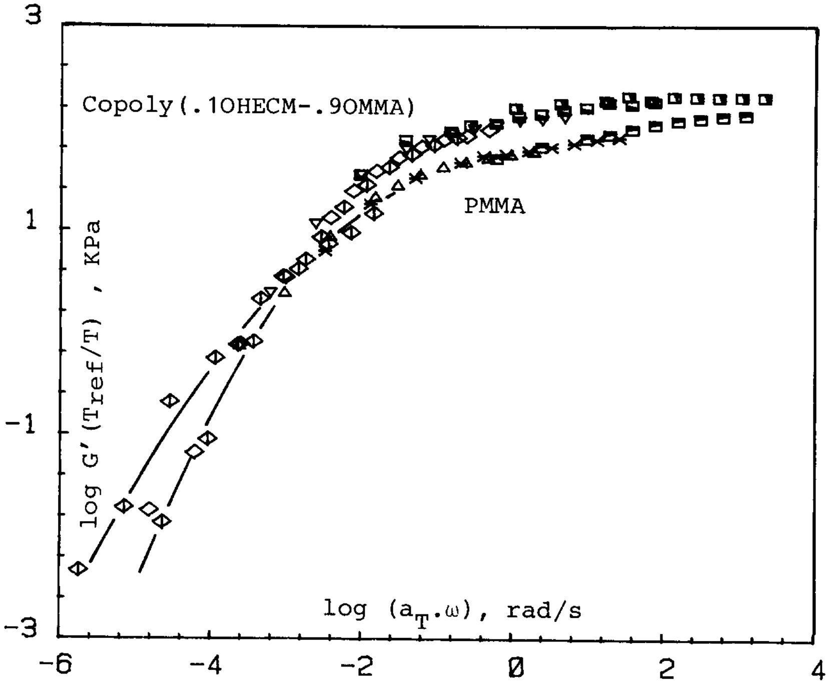

Figure 2: Master curves of the storage modulus of PMMA and of Copoly(.10HECM-.90DNBM). $T_{ref} = T_g + 90$ K

In Figure 3 the master curves of the storage moduli of the complementary components, Copoly(.10HECM-.90MMA) and Copoly(.10DNBM-..90MMA), as well as their 1:1 polyblend are plotted. For comparison the dotted line presents the master curve of the 1:1 blend of the blend Poly(HECM) - Poly(DNBM), the components consisting of donor and of acceptor subunits exclusively. Despite one order of magnitude lower concentration of complexing units the former polyblend holds quite identical storage modulus at low frequencies and high temperatures, more than one order of magnitude higher than that of the components. Evidently, between statistical chains the relative probability of reinforcing charge transfer contacts diminishes with the concentration of groups capable for interaction. Work is in progress to optimize donor-acceptor complexation with the aim to minimize the concentration of interacting groups as well as the molecular weight of the components. Low melt viscosity and high modulus over a broad range of temperatures and frequencies is the objective of this approach. Theoretical considerations concerning the probability of charge tranfer contacts between statistically coiled backbones may be helpful in this connection. For donor-acceptor complexed poly(butyl methacrylate)s experimental data concerning minimization of interacting groups are presented at the end of this paper.

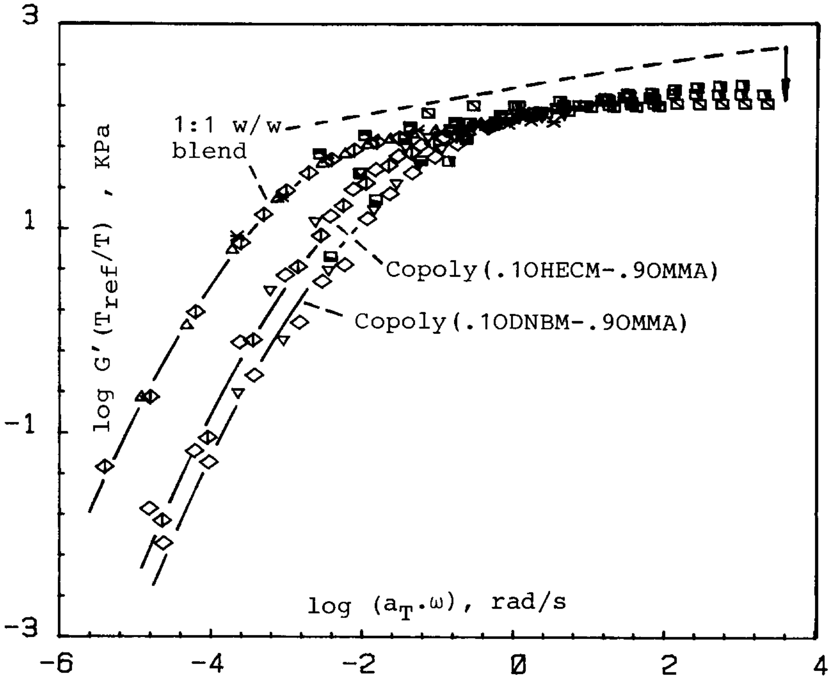

Figure 3: Master curves of the storage modulus of Copoly(.10HECM-.90MMA), Copoly(.10DNBM-.90MMA) and of the 1:1 w/w polyblend of both components. The dotted line gives the master curve of the 1:1 w/w blend Poly(HECM-Poly(DNBM) [2], shifted +.5 along the ordinate

The pronounced network character of the blends containg .10 interacting groups is confirmed too by the dynamic viscosity data, as shown in Figure 4. The zero shear viscosity of the blend exceeds significantly that of the components, and it is reached at lower frequencies.

Finally, donor-acceptor complexation of poly(butyl methacryl-

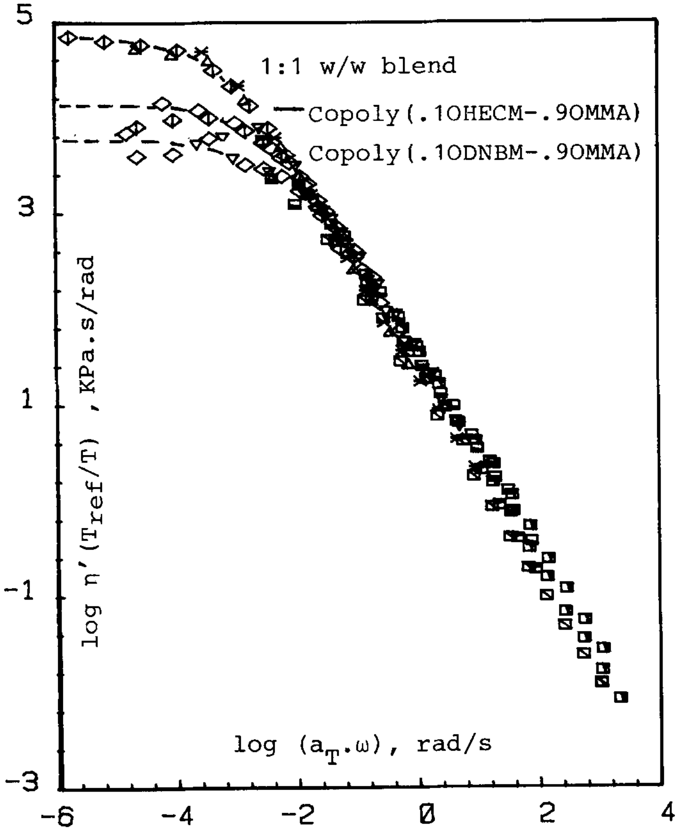

Figure 4: Master curves of the dynamic viscosity of Copoly(.10HECM-.90MMA), Copoly(.10DNBM-.90MMA) and of the 1:1 w/w polyblend of both components

ate)s may be discussed. Figure 5 demonstrates that the increase in the high temperature low frequency modulus due to complexation by blending is somewhat less pronounced than for the modified poly(methyl methacrylate)s discussed before. This may be the consequence of the increased steric effect of the more extended butyl side groups. Figure 6, however, shows that the thermoreversible reinforcing effect remains practically unaffected, when the portion of one of the complexing partners is reduced by a factor of 10 (donor HECM in this case). Evidently, the probability of mechanically relevant contacts is not reduced drastically. A 1:1 polyblend containing .03 each of the complexing units within the complimentary chains may exhibit practically identical mechanic dynamical behaviour.

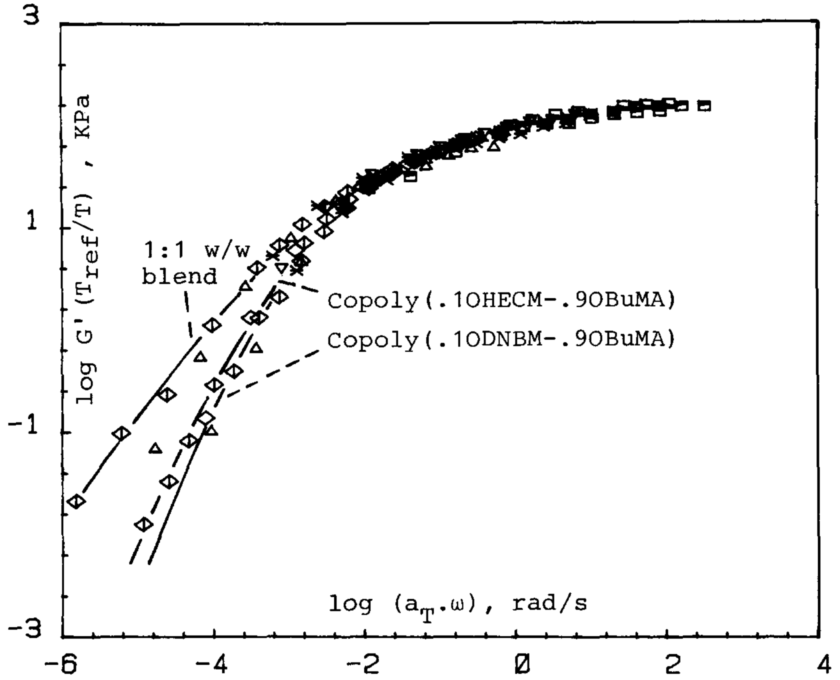

Figure 5: Master curves of the storage modulus of Copoly(.10HECM-.90BuMA), Copoly(.10DNBM-.90BuMA) and of the 1:1 w/w polyblend of both components

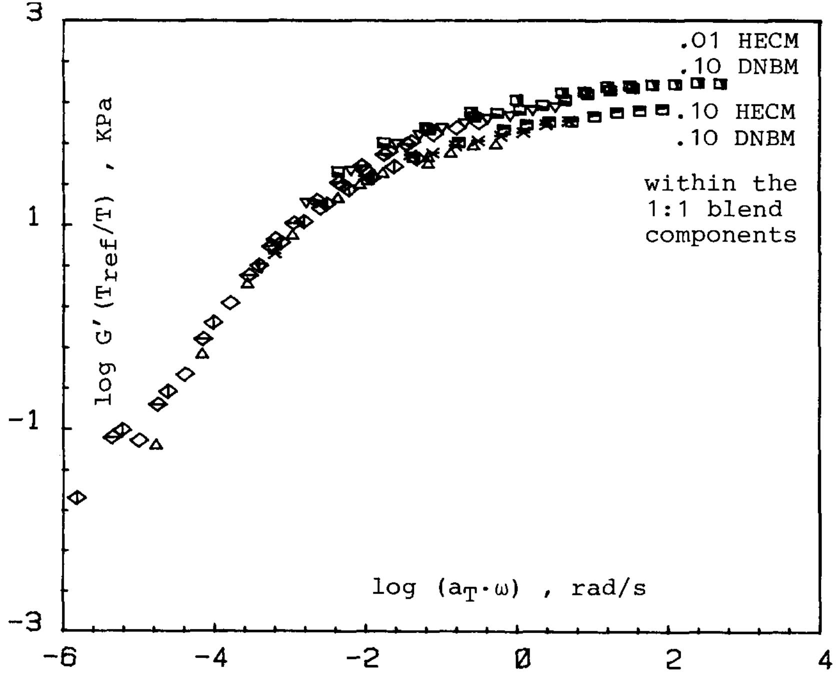

Figure 6: Master curves of the storage modulus of the 1:1 w/w polyblends of Copoly(.01HECM-.99BuMA)-Copoly(.10DNBM-.90BuMA) (upper curve, shifted +.25) and of Copoly(.10HECM-.90BuMA)-Copoly(.10DNBM-..90BuMA) (lower curve)

In conclusion the obtained viscoelastic data on donor-acceptor complexed poly(methyl methacrylate)s as well as poly(butyl methacrylate)s confirm the strategy to design thermoreversibly reinforced macromolecular systems and encourage optimization of the effect. The weak point of the complexed blends consisting on donor and acceptor subunits exclusively [2], their unsufficient thermal stability, has been overcome by the complexed copolymers containing low portions of interacting groups without critical loss of the mechanic dynamical niveau.

The question remains open, wether it is obligatory to maintain the principle of intermolecular complexation, when the concentration of the interacting units within the chains reaches a critical lower level. If the average distance of complexing subunits exceeds a certain value, it may be irrelevant, wether they are arranged within different or within the same macromolecule. This critical minimum average distance should be frequency dependent, in consequence of the frequency dependence of the segment volume relevant for the mechanical processes.

ACKNOWLEDGEMENTS

Financial support by ARBEITSGEMEINSCHAFT INDUSTRIELLER FORSCHUNGSVEREINIGUNGEN and by VERBAND DER KUNSTSTOFFERZEUGENDEN INDUSTRIE is gratefuly acknowledged. Mr. U. BANDARA we thank for the LAXR measurements.

REFERENCES

1. PERCEC, V., NATHANSON, A. and SIMIONESCU, C. I., Polymer Bulletin 5, 217, 225 (1981)

SIMIONESCU, C. I., PERCEC, V. and NATHANSON, A., Polymer Bulletin 3, 535 (1980)

SIMIONESCU, C. I., NATHANSON, A. and PERCEC, V., Polymer Bulletin 3, 543 (1980)

2. SCHNEIDER, H. A., CANTOW, H.-J. and PERCEC, V., Polymer Bulletin 6, 617 (1982)

3. FERRY, J. D., Viscoelastic Properties of Polymers, III. Ed. Wiley, New York, 274 (1980)

4. MILLER, A. A., J. Polymer Sci A2, 1095 (1964)

Accepted April 28, 1982
C