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Interrelations between constitution, configuration and conformation in chlorinated polyalkenamers

2. Interaction effects in solution and in polymer blends

U. Licht and H.-J. Cantow**

Institut für Makromolekulare Chemie der Universität Freiburg, Stefan-Meier-Strasse 31,
D-7800 Freiburg, Federal Republic of Germany

SUMMARY

The FTIR-intensity ratio of C-Cl anti and C-Cl gauche vibrations in head-to-head chlorinated polymers seems to be a function of the conformational equilibrium and is modified by the polarity of the surrounding of the dipoles. Solvent effects, specific interactions with plasticizers and blend partners can be detected in the FTIR-spectra of of chlorinated compounds and C=O containing molecules. In the behaviour towards plastcizers and polybutylmethacrylate differences are observed between the degrees of chlorination (polarity) and the configurations of the head groups (stereochemical contribution to specific interactions). A trend to stronger self-contacts with lower polarity from head-to-head polyvinylchloride to poly dichloro octamethylene is found. This corresponds to a decrease of plasticizer and polar solvent influence, as well as to miscibility with polybutylmethacrylate.

INTRODUCTION

The chlorinated polyalkenamers with head-to-head structure allow investigations depending on polarity (variable CH_2- part) and stereochemistry (threo and erythro HH). They are not only model substances for PVC and chlorinated polyethyene, but also models for an investigation of the role of configuration and polarity on specific interactions in polymers. These specific interactions are often discussed to be the reason for plasticizer effects or miscibility in blends. In this paper two representatives of high and low degree of chlorination are examined with respect to the influence of isobutyricacid-butylester (IBBE, polar model for PBMA), o-xylene (nonpolar), plasticizer dinonylphthalate (DNP), atactic PBMA, PMMA and low molecular polycaprolactone (PCL). One threo and one erythro sample are compared.

EXPERIMENTAL

Synthesis of chlorinated polyalkenamers, taking of spectra and sample preparation are described above. HH-chlorinated samples are poorly soluble. The absorption of the solvent in the fingerprint region exceeds those of the polymer extremely. Therefore swollen samples were used instead of solutions. Thin films of the polymer on KBr-plates were swollen in a large amount of solvent, after evaporation of the exess solvent the spectra were taken. The amount of solvent was calculated from the weight difference between film and mixture. Blends and plasticized samples were cast from THF solutions and dried in vacuo. Difference spectra were constructed by subtracting the spectra of the pure component from the mixture. In the case of PBMA the vibration at 530 cm^{-1}, in o-xylene the 742 cm^{-1} vibration, in isobutyricacid-butylester the band at 510 cm^{-1}, in the plasticizer the vibration at 1600 cm^{-1} were used to subtract the partner spectrum.

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*Prof. Dr. Paul Rempp zum 60. Geburtstag herzlichst gewidmet

**Present address: BASF AG, D-6700 Ludwigshafen, FRG

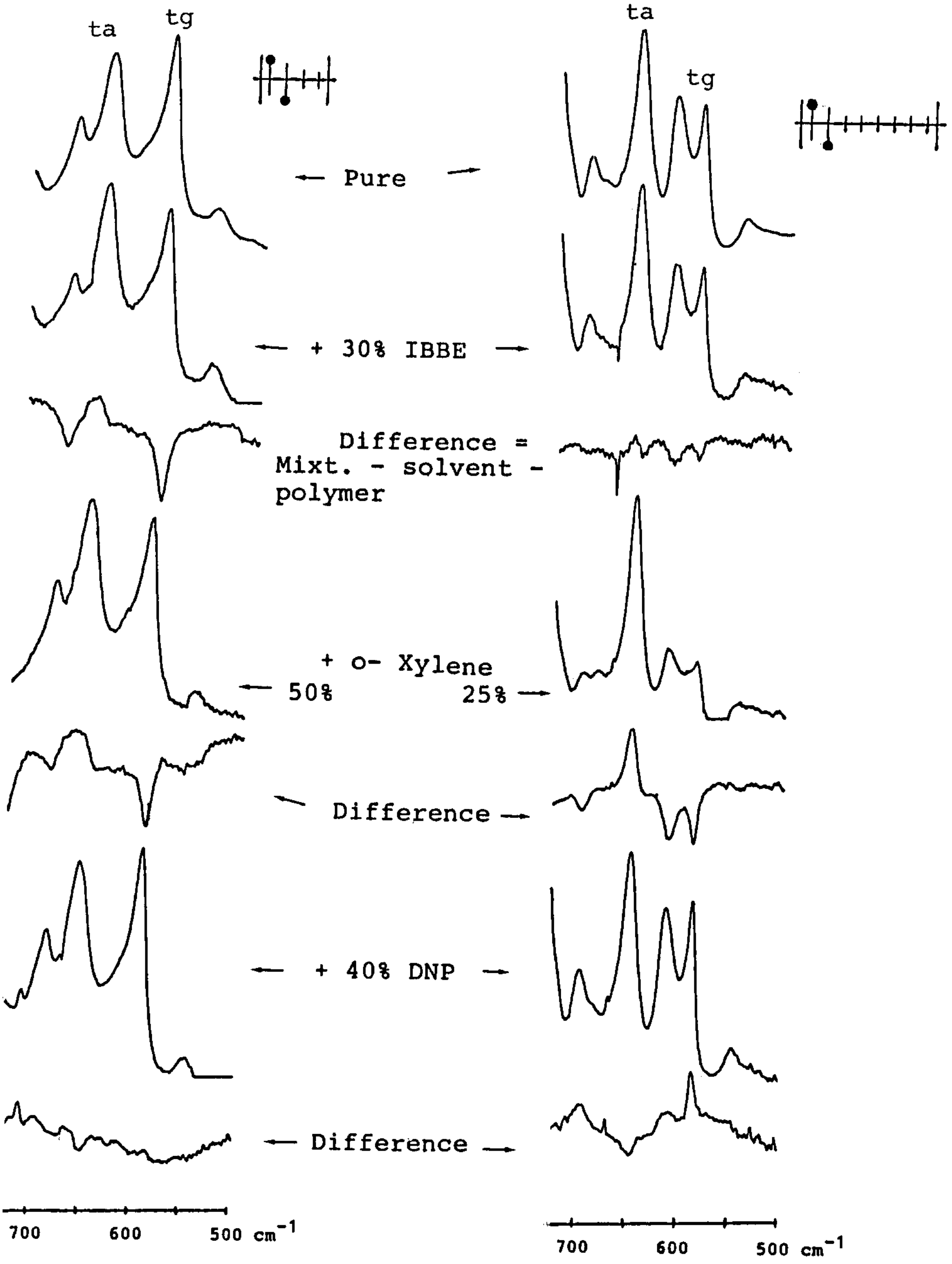

Fig. 1: Solvent and plasticizer effects on C-Cl-vibrations of t-PDCTM and t-PDCOM

RESULTS AND DISCUSSION

1) Solvents and Plasticizers

The C-Cl anti vibration at 650 cm^{-1} and the C-Cl gauche band at 595 cm^{-1} (595, 613 cm^{-1} resp. for PDCOM) are indicators for specific interactions. Their intensity reacts sensitively to changes in polarity. In Fig.1 the influence of IBBE, o-xylene and DNP is shown for the two degrees of chlorination. In HH-PVC the two solvent show only gradually different results. The intensity ratio in the conformation bands increases with concentration of solvent. In the PDCOM the ester and the plasticizer have only small influence on the spectrum, the nonpolar o-xylene is preferred and disturbs the polymer structure. The plasticizer does not affect the PVC spectrum. The electronic situation of the C-Cl-groups is unchanged. But the C=O vibration of DNP is broadened and shifted to lower wavenumbers, a typical sign for H-bonding like interactions, found also in dibutylphthalate/HT-PVC mixtures (2) (Fig. 2). This is not observed in the PDCOM mixture.

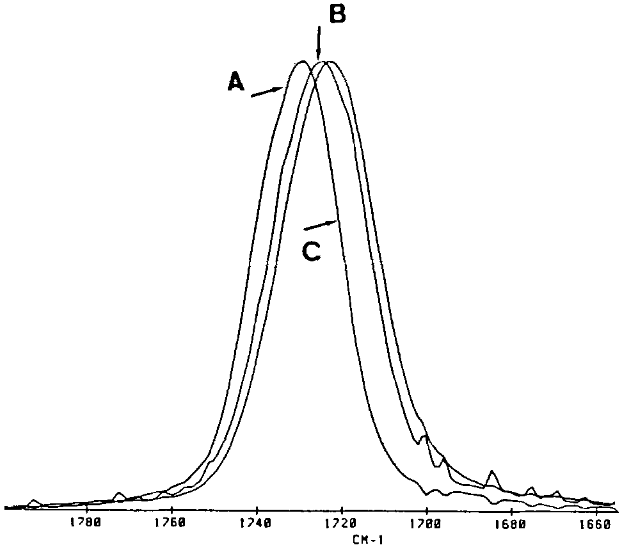

Fig. 2: C=O vibration of plasticizer - A: +0%, B: +60%, C: +80% PDCTM

We conclude, that in the high chlorinated, high polar and stiff material self contacts are not specific and are from polymer-solvent contacts. This contact may be of dipolar type, of the negative and positive partial charges, or like H-bondings between the acidic methine H atom and the carbonyle group. The plasticizer shows interactions with the chlorinated part, but it is not able to separate the chains completely like the solvents. With unaffected intenssity, the polymer remains in a similiar surounding as in the glassy state. In the low chlorinated polymer the flexible CH$_2$ part makes strong specific interactions between the C-Cl-dipoles possible, states of order exist. In the competition between self-contacts and specific polymer-polar solvent interactions the polymer-polymer contacts win. The nonpolar solvent attacks in the long CH$_2$-tail, solvation of this part forces the chains to separate without dipol-dipol interactions. In erythro polymers no signific-ant spectral changes are observed. The all-anti vibration is insensitive to solvent effects.

2) Blends

This explanation can be transferred to the blend behaviour. Threo dichlorotetramethylene seems, to be miscible with PBMA in a concentration range of 20%-80% HH-PVC. The same intensity changes with increasing concentration PBMA are found, as well as frequency shifts in PBMA. (Figs. 3 and 4).

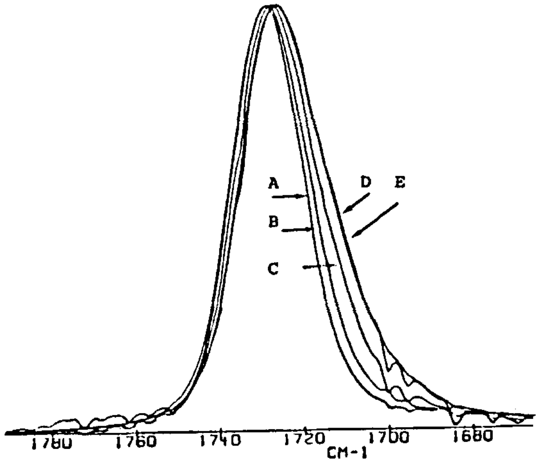

Fig. 3: Frequency shift and broadening of the C=O band of PBMA with increasing concentration of t-PDCTM
A: +0%, B: +20%, C: +40%, D: +60%, E: +80% t-PDCTM

In the HH-PVC/PCL blend the C=O-vibration of the crystalline part vanishes (Fig. 5). The broadening of the carbonyle vibration in PBMA with HH-PVC concentration is shown in fig. 6, around 60 w.-% chloro component (∿ 1:1 molar ratio) a favorable mixture for dipolar contacts is reached. For HT-PVC/PCL blends a s-shaped curve is found as sign for increasing interactions (1)

Blends of threo PDCOM with PBMA or PCL are obviously phase separated. The microcrystalline structure of PDCOM remains. The spectrum is slightly affected in the C-Cl-region, perhaps due to phase boundary interactions. Further a tendency to miscibility in the amorphous part may be the reason The C=O vibration of PBMA shows no changes in frequency or shape (Fig. 3) Specific interactions as discussed above are not probable. In the high polar chloro component directed dipolar contacts to other segments are not possible for all head-groups because of the immobility due to rotaional restriction. Miscible blends exist as competition between self- and specific interactions with carbonyl groups. In low chlorinated polymers (no steric hindrance of adjacent head-groups) arrangements of C-Cl-dipoles to ordered structures cause strong homo contacts not to be opened by hetero interactions.

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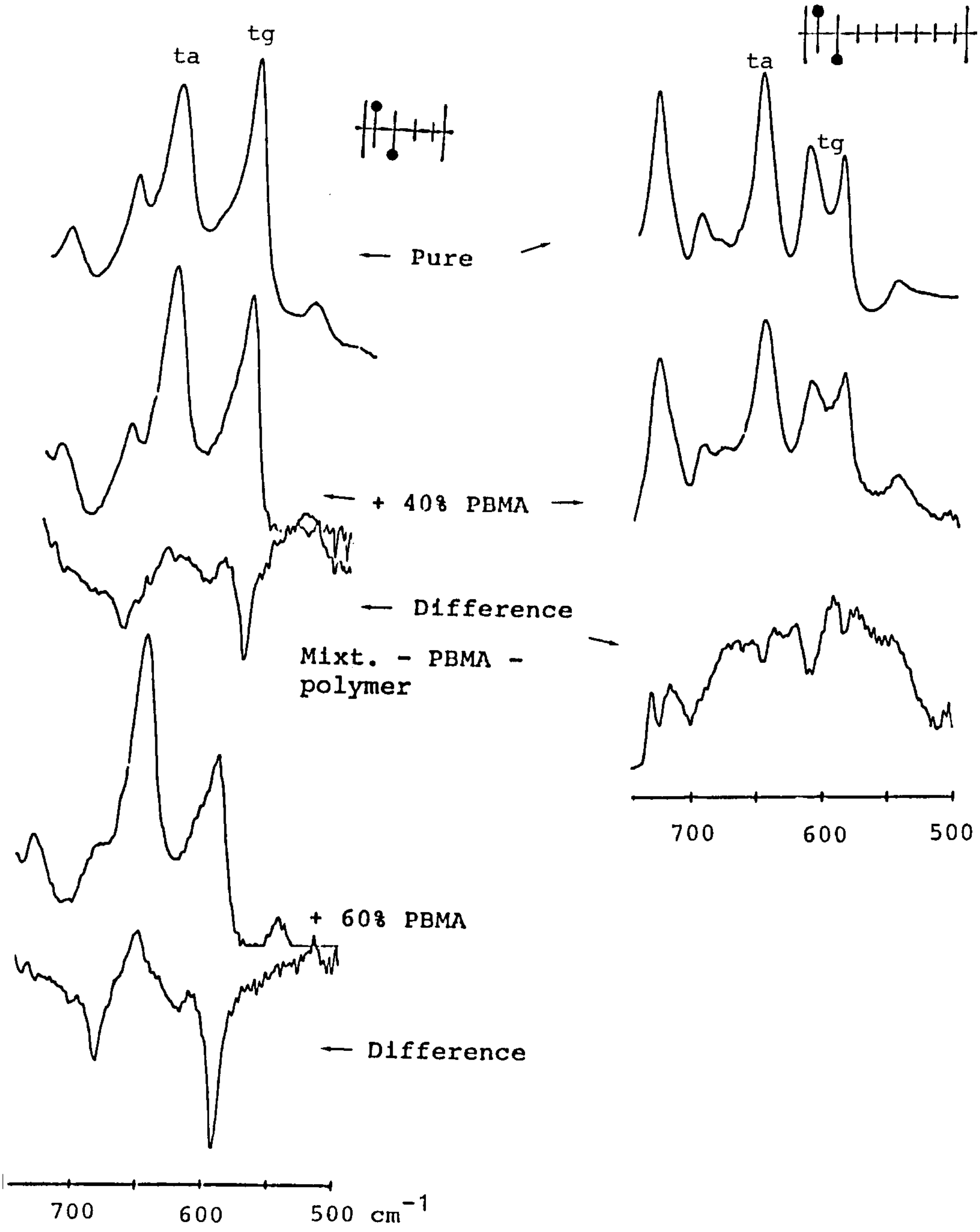

Fig. 4: Changes of C-Cl-vibrations of t-PDCTM and t-PDCOM in blends with PBMA

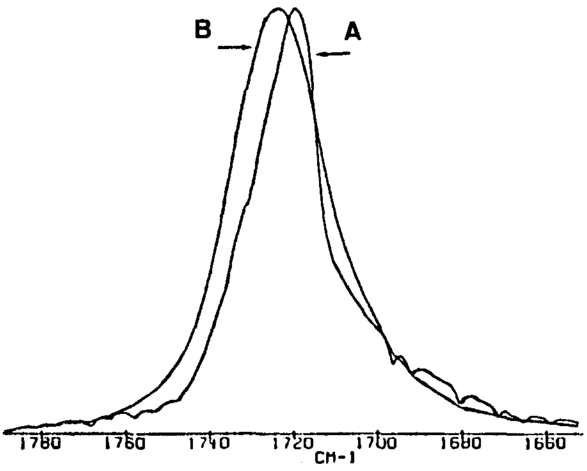

Fig. 5: C=O vibration of partially crystalline PCL
A: pure, B: blend with 80% HH-PVC

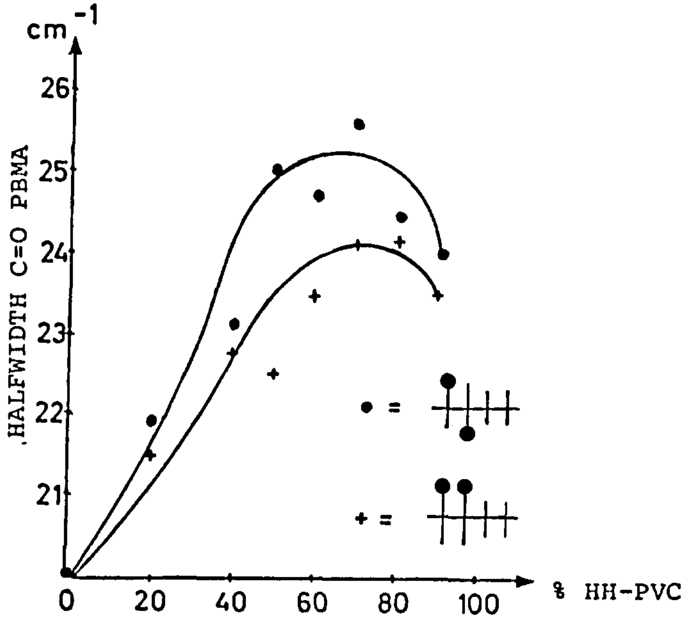

Fig. 6: Halfwidth of carbonyl vibration in PBMA with increasing content of HH-PVC in the blend

REFERENCES

1) M. M. Coleman and J. Zarian, Polym. Sci., Polym. Phys. 17, 837 (1979)

2) E. Benedetti, F. Posar, A. D'Alessio, P. Vergamini
J. Polym. Sci. 23, 1187 (1985)3)

3) D. L. Tabb and J. L. Koenig, Macromolecules 8, 929 (1975)

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