Constitutional and Configurational Influences on the Viscoelastic Data of Methyl Substituted Hydrocarbon Macromolecular Systems

1. Non-Entangled Atactic Head-To-Tail and Inverted Polypropylenes

H.A. Schneider and H.-J. Cantow

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

S U M M A R Y

From viscoelastic measurements on the melts of non-entangled atactic head-to-tail and of head-to-head - tail-to-tail poly-propylenes over a broad region of temperatures and frequencies it is concluded that the head-to-tail macromolecules are the significantly less mobile ones. Equimolar blends of both com-ponents show up one-phase behaviour. A tendency towards beginn-ing incompatibility may be concluded, however, from some char-acteristics of the blend: Additional transition in the glassy state, at 210.3 K, increased fractional free volume and raised zero shear melt viscosity.

I N T R O D U C T I O N

The isomeric polypropylenes offer unique chances to investigate systematically the interrelations between the molecular arrange-ment (constitution and configuration), the micro- and the macro-conformations and the physical as well as the applicational properties. Without modifying the chemistry of the substituents it is possible to synthesize macromolecules which despite their identical subunits, $-CH_2-$ and $-\overset{CH_3}{\underset{}{CH}}-$, show up different sequent-ial arrangement and properties, consequently. Three types of triads may occur within regular polypropylenes,

isotactic, syndiotactic and

heterotactic. The ditactic inverted polypropylenes, poly(1,2-dimethyltetramethylene)s, exhibit increased variety of sequences,

⌇⌇+↑↑++↑↑++↑↑+⌇⌇ erythrodiisotactic, ⌇⌇+↑↑++↑↑++↑↑+⌇⌇ erythro-
disyndiotactic and ⌇⌇+↑↓+++↑↓+++↑↓+⌇⌇ diatactic, e. g.

Macromolecules of such types have been investigated intensively
with respect on the consequences of constitution and configurat-
ion on the conformation and on the dynamics at segmental level by
^{13}C-NMR techniques, in solution under fast exchange and on low
molecular weight representative analogs under slow exchange
conditions [1-8], as well as in the solid state [9] [10]. Consequ-
ently, it seemed to be interesting to investigate the influence
of the microstructure on the viscoelastic properties. Amorphous
samples have been preferred in order to avoid dominant inter-
molecular interactions present within semicrystalline samples.

Furthermore, it was the intention of our studies to elucidate
wether there are tendencies towards incompatibility in mixtures
of atactic head-to-tail with diatactic inverted polypropylenes,
irrespective the fact that they are built up by identical sub-
units.

When comparing the two types of polypropylenes under investig-
ation - ht and hh-tt - it is evident that the ht-macromolecules
exhibit one type of bond only within the backbone, $-CH_2-\overset{CH_3}{\underset{1}{CH}}-$,
whereas the hh-tt-macromolecules show up two addit-
ional types, $-CH_2-CH_2-$ and $-\overset{CH_3}{\underset{CH_3}{CH}}-\overset{CH_3}{\underset{CH_3}{CH}}-$. Significant consequen-
ces on the viscoelastic behaviour may be caused by these struct-
ural characteristics.

It is evident that investigations on regular and on inverted po-
lypropylenes of different tacticity offer the chance to clarify
the structure - conformation - properties interrelations of
ethylene-propylene copolymers of arbitrary sequence structure
and, in a later state of the studies, of other ethylene-α-olefin
copolymers. Work is in progress on model macromolecules for ethy-
lene-propylene copolymers, ⌇⌇++++↑↓++++⌇⌇ and ⌇⌇++++++↑↓++++++⌇⌇ , e.g.

E X P E R I M E N T S   A N D   D I S C U S S I O N

For the reported studies samples have been choosen whose molec-
ular weights just did not exceed the critical length causing
entanglements: Vapor pressure osmometry yielded $M_n = 7300$ for

the atactic ht-polypropylene and M_n = 8500 for the diatactic hh-tt-polypropylene. Comparable molecular heterogeneity was ascertained by gel permeation chromatography.

Equimolar mixtures of both the components have been prepared by evaporation from benzene solution as well as by freeze drying from p-xylene solution. Both procedures turned out to be equivalent.

Glass transitions were measured with the PERKIN ELMER DSC-2 Differential Scanning Calorimeter, using heating rates from 2.5 to 20° min^{-1} and extrapolating to zero rate. The DSC studies evidenced compatibility of both types of polypropylenes with the molecular weights cited above, the DSC curves exhibiting one single glass transition, irrespective the heating rate. For zero heating rate the T_g's were 259.5 K for the ht-polypropylene, 242.3 K for the hh-tt-polypropylene and 247.0 K for the equimolar blend. These data have been confirmed by thermomechanical measurements, using a PERKIN ELMER TMS-2 at a heating rate of 10° min^{-1}: 260.8 K for the ht-PP, 246.3 K for the hh-tt-PP and 252.3 for the equimolar blend. Only in the mixture, however, an additional γ-transition has been verified in the glassy state, at 210.3 K.

Viscoelastic measurements in the melt were executed with the INSTRON Model 3250 Rotary Rheometer within the temperature range from 314 to 394 K, using the orthogonal, excentric rotating disks, mode. Frequencies have been varied between $9 \cdot 10^{-3}$ and $2 \cdot 10^{+2}$ rpm.

Figures 1 and 2 represent the master curves of the storage modulus, $G'(\omega)$, and of the dynamic viscosity, $\eta'(\omega)$, versus the frequency, ωa_T, on a double logarithmic scale. Experimental shift factors were corrected according to WILLIAMS, LANDEL and FERRY [11] with the reference temperature T_g + 75 K for all samples.

The following constants of the WLF equation have been determined from the dynamic viscosity data for the components and for their mixture:

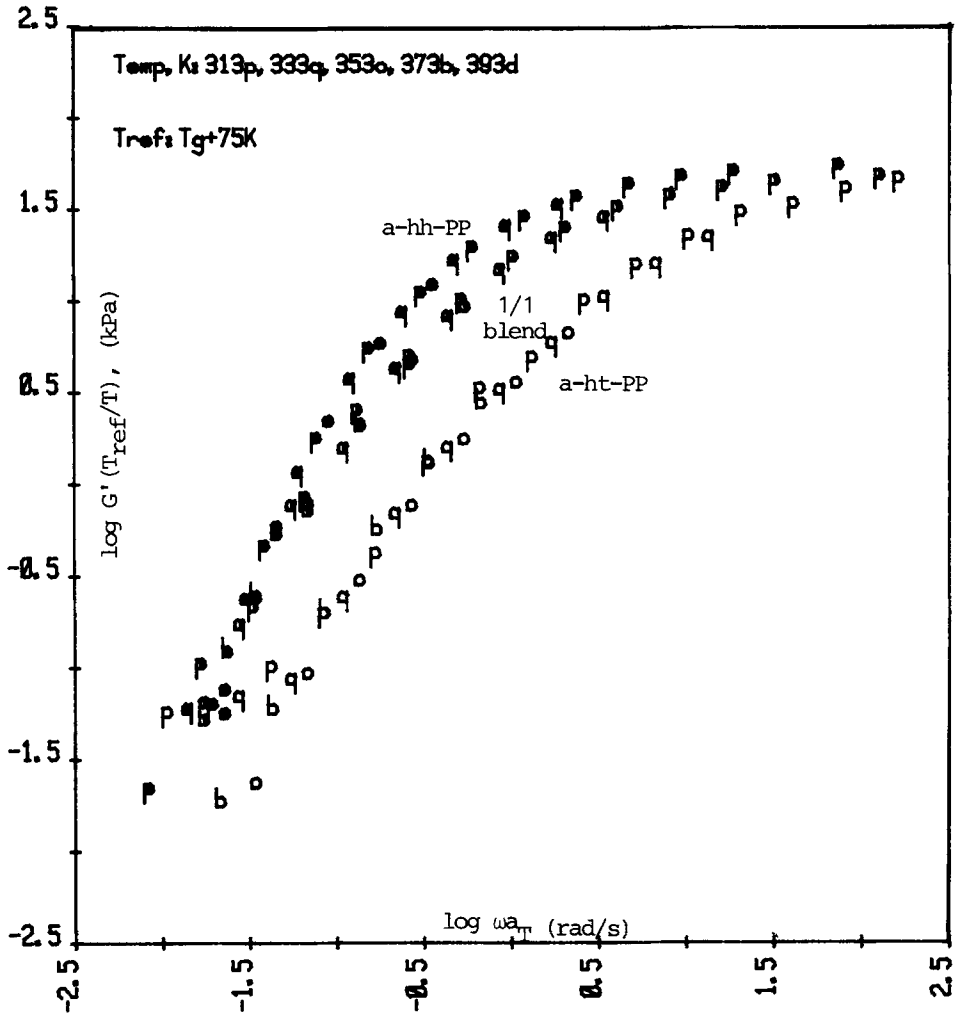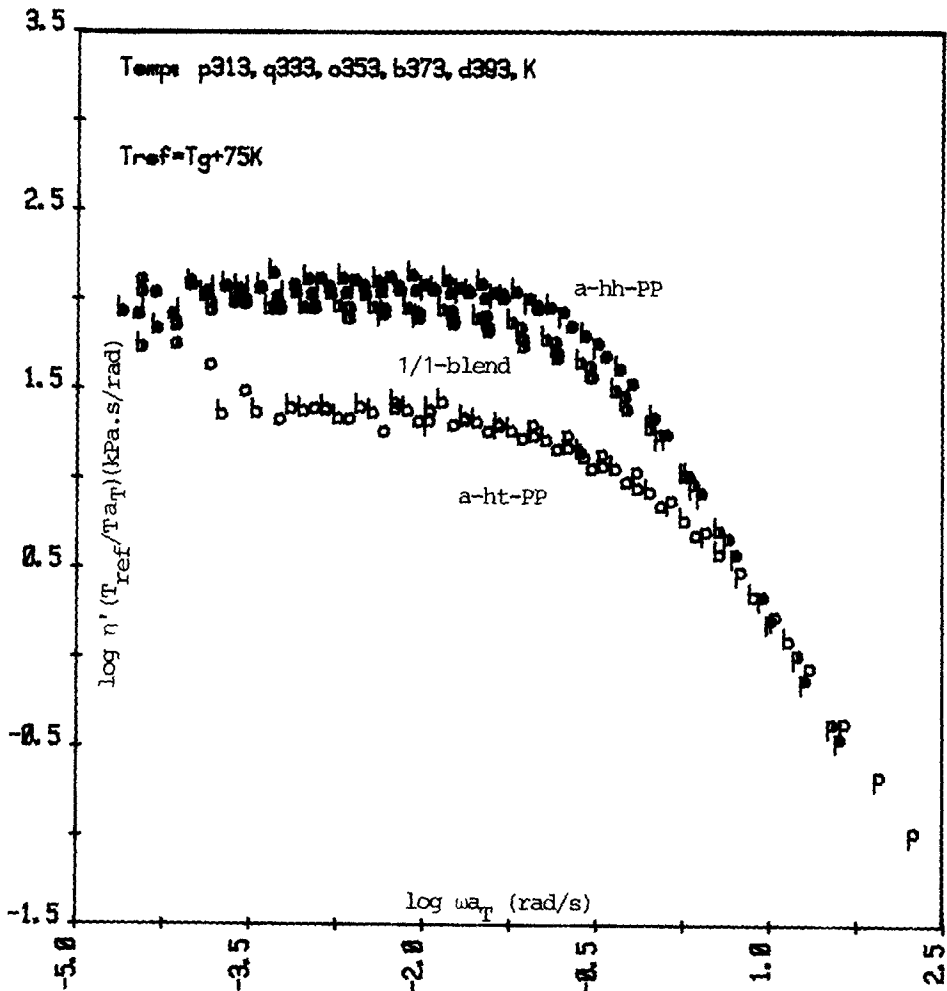|	atactic ht-PP	diatactic hh-tt-PP	equimolar mixture
c_1	5.30	6.19	8.49
c_2	115.4	119.1	166.8

Figure 1: Master curve of the storage modulus of atactic ht-polypropylene (a-ht-PP), diatactic hh-tt- polypropylene (a-hh-PP) and the equimolar mixture (1/1 blend)

The apparent activation energies of the zero shear flow have been calculated as 86.4 kJ mol^{-1} for the atactic ht-PP, as 80.8 kJ mol^{-1} for the diatactic hh-tt-PP and as 84.6 kJ mol^{-1} for the equimolar mixture.

From the data reported the following characteristics of both the types of atactic polypropylenes and of their equimolar mixture are evident:

1. Because of its lower glass transition temperature the in-
verted polypropylene exhibits higher mobility as the "normal"
polymer. Since the T_g of the mixture is situated nearer to that
of inverted polypropylene, the head-to-tail macromolecules seem
to be mobilized by the presence of the second component. The
additional γ-transition of the mixture may be discussed within
this context.

2. The inverted polypropylene shows up only 70 % of the zero
shear melt viscosity per propylene unit, when compared with the

Figure 2: Master curve of the dynamic viscosity of atactic ht-
polypropylene (a-ht-PP), diatactic hh-tt-polypropylene (a-hh-PP)
and the equimolar mixture (1/1 blend)

regular polypropylene. Up to now it was not possible, however, to discriminate to which extent the coil dimensions and the monomer friction coefficient, respectively, are responsible for the different melt viscosities of both species. The mixture of the components shows up a zero shear viscosity at temperatures higher than the reference temperature, which is higher than expected according to mixing rules. Evidently, the mobility of the inverted sequence macromolecules is hindered by the presence of the less mobile chains of regular polypropylene. Apparently, the influences of the components relative to each other reverse around the reference temperature.

3. The apparent activation energy of zero shear flow is lower for the inverted polypropylene when compared with that of the regular one. For the mixture this energy is not far from that of the head-to-tail polypropylene. The deviations from additivity are not drastic, however. Experimental shift data suggest substantially higher C_1 and C_2 constants of the WLF equation for the studied blend.

In the following an attempt is made to interprete the behaviour of the mixture in terms of the free volume concept.

Introducing the DOOLITTLE equation for the viscosity of a liquid [12]

$$\log \eta_O = \log A + \frac{B}{2.3} (v_O/v_f) \qquad\qquad (1)$$

into the WLF expression the constants C_1 and C_2 become $C_1 = B/2.3\, f_{ref}$ and $C_2 = f_{ref}/\Delta\alpha_f$, respectively, with f the fractional free volume $f = v_f/(v_O + v_f) \simeq v_f/v_O$ at T, f_{ref} and f_g those at the reference temperature and at T_g, respectively. $\Delta\alpha_f$ is the difference of the thermal expansion coefficient of the fractional free volume below and just over T_g . v_O and v_f denominate the specific occupied and the specific free volume available to the system, respectively.

Usually f_g is assumed to exhibit a constant value (0.025), as well as $\Delta\alpha_f$. This can not apply, however, for the present system, because in the mixture both C_1 and C_2 show up higher values than for the components. Consequently, $\Delta\alpha_f$ should vary. Thus $\Delta\alpha_f$ has been determined by TMA for both the components and the mixture. The Table presents the experimental $\Delta\alpha_f$'s

and f_{ref} , calculated with C_2 from the experimental shift data.

Table I: Expansion coefficients, fractional free volumes and
B for the polypropylenes and their equimolar blend

	$\Delta\alpha_f \cdot 10^4$	f_{ref}	f_g	$B=2.3f_gC_{1,g}$
diatactic hh-tt-PP	5.77	0.071	0.025	0.98
atactic ht-PP	5.45	0.063	0.022	0.77
equimolar blend	5.96	0.099	0.054	1.92

$$f_{ref} = C_2\Delta\alpha_f \quad f_g = f_{ref} - \Delta\alpha_f(T_{ref} - T_g)$$
$$C_{1,g} = C_1C_2(C_2 - (T_{ref} - T_g))$$

In the third column f_g is evaluated. With these f_g's the B's
in the fourth column are calculated.

The obtained data suggest:
A substantially higher fractional free volume is found in the
blend, about double the "universal" value of .025, which is
effective in the components. In parallel, the B constant of
the blend is approximately doubled. The increase of the fract-
ional free volume in the blend has been confirmed independently
by density measurements at 303 K: 0.871 for diatactic hh-tt-PP,
0.879 for atactic ht-PP and 0.856 for the equimolar mixture.
The free volume increase might be interpreted by a tendency
of onsetting phase separation. The assumption may be reason-
able that part of the free volume in the binary system is built
up already at the additional γ-transition. Assuming consequent-
ly T_γ as the mobility active transition, modified constants may
be derived: $\Delta\alpha_f=6.86\cdot10^{-4}$, $f_g=0.037$ and B=1.31. Thus the
fractional free volume in the blend approaches the universal
value by this treatment. So the assumption of a mobilization
of the ht-chains in the presence of the mobile hh-tt-macro-
molecules appears feasible by the two arguments, the decreased
T_g of the blend as well as the T_γ transition.

At temperatures above T_{ref} apparently the higher fractional
free volume of the blend is accompanied by stiffening of the
chains, as evidenced by the increased zero shear viscosities.

It may be noted that the storage modulus is affected also as shown in Figure 1.

Work is in progress to correlate the dynamic-mechanical data with conformational analysis at segmental level, carried out with ^{13}C-NMR.

R E F E R E N C E S

1. ELGERT, K.-F., RITTER, W. and CANTOW, H.-J., Chemiker-Ztg. 101, 297 (1977)

2. ELGERT, K.-F. and RITTER, W., Makromol. Chem. 178, 2827 (1977)

3. ELGERT, K.-F. and RITTER, W., Makromol. Chem. 178, 2857 (1977)

4. RITTER, W., HULL, W. E. and CANTOW, H.-J., Tetrahedron Lett. 34, 3093 (1978)

5. RITTER, W., MÖLLER, M. and CANTOW, H.-J., Makromol. Chem. 179, 823 (1978)

6. RITTER, W., MÖLLER, M. and CANTOW, H.-J., Polymer Bulletin 2, 533 (1980)

7. MÖLLER, M., RITTER, W. and CANTOW, H.-J., Polymer Bulletin 2, 543 (1980)

8. MÖLLER, M., RITTER, W. and CANTOW, H.-J., Polymer Bulletin 4, 609 (1981)

9. MÖLLER, M. and CANTOW, H.-J., Polymer Bulletin 5, 119 (1981)

10. GRONSKI, W., HASENHINDL, A., LIMBACH, H. H., MÖLLER, M. and CANTOW, H.-J., Polymer Bulletin 6, 93 (1981)

11. WILLIAMS, M. L., LANDEL, R. F. and FERRY, J. D., J. Amer. Chem. Soc. 77, 3701 (1955)

12. DOOLITTLE, A. K., J. Appl. Phys. 23, 236 (1952)

C