ELSEVIER

Polymer 42 (2001) 8753–8757

polymer

www.elsevier.com/locate/polymer

Rheological properties of poly(trimethylene 2,6-naphthalenedicarboxylate) melts

U. Stier, D. Schawaller, W. Oppermann*

Institute for Man-Made Fibers, Körschtalstrasse 26, 73770 Denkendorf, Germany

Received 23 March 2001; received in revised form 30 May 2001; accepted 5 June 2001

Abstract

The rheological properties of poly(trimethylene naphthalene-2,6-dicarboxylate) (PTN) were studied using a dynamic stress rheometer with oscillatory parallel plates. The influence of temperature and molecular weight on the storage modulus, loss modulus, and complex viscosity was investigated. It was possible to express the temperature dependence of the shift factors a_T with the Arrhenius equation; the activation energy was found to be 85 kJ/mol. A comparison of molecular weight determined: (a) by rheological measurements and (b) by Mark–Houwink–Sakurada equation showed excellent agreement. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(trimethylene naphthalene-2,6-dicarboxylate); Rheological properties; Mark–Houwink–Sakurada equation

1. Introduction

Poly(ethylene terephthalate) (PET) has received rapidly growing interest during the last several decades. Nowadays further polyesters have become commercially available: Besides poly(butylene terephthalate) (PBT) and the recently introduced poly(trimethylene terephthalate) (PTT) [1–5], both with markedly higher resilience than PET, poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) was commercialized as a polyester having enhanced thermal and hydrolytic stability [6–8].

A relatively unknown polyester within the family of poly(alkylene naphthalates) is poly(trimethylene 2,6-naphthalenedicarboxylate) [9–12] (PTN) (see Fig. 1). We have studied the synthesis of PTN in detail [13,14]. In the present paper, we will focus on the rheological properties of PTN melts and their dependence on temperature and molecular weight. Such data are of great interest not only in quality control, but also in designing suitable processing conditions.

Rheological investigations of aromatic polyester melts are difficult because of the high temperatures required and the tendency of the materials to degrade or change under such conditions. Polyesters are specifically prone to hydrolytic or oxidative chain scission as well as to pyrolytic scission (*cis*-elimination) [15,16]. On the other hand, post-condensation reactions can also occur. This may be the reason for the wide range of different results found e.g. in the literature on PET viscosities [17–21]. The present paper will clearly show the boundaries of temperature dependent measurements in the case of PTN and describe experimental methods to minimize degradation processes.

2. Experimental

2.1. Preparation and characterization of PTN

PTN was prepared by transesterification of dimethyl 2,6-naphthalenedicarboxylate (2,6-DMN) with 1,3-propanediol followed by polycondensation using Ti(IV)butylate as catalyst. A detailed description of the synthesis of PTN can be found elsewhere [13,14]. The rheological investigations were performed on 4 polymers differing noticeably in molecular weight. Some characteristic properties of these are listed in Table 1.

2.1.1. Solution viscosity

The determination of relative solution viscosity η_{rel} of PTN was performed by dissolving 1 g of PTN in 100 ml phenol/1,1,2,2-tetrachloroethane (1:1; w/w). The measurements were carried out at 20°C using a Ubbelohde-type viscometer. The intrinsic viscosity $[\eta]$ was determined by extrapolating the reduced viscosity η_{red} to zero concentration. From the slope of a plot of η_{red} vs. concentration, the

* Corresponding author.
E-mail address: wilhelm.oppermann@itc.itvd.uni-stuttgart.de (W. Oppermann).

PII: S0032-3861(01)00448-7

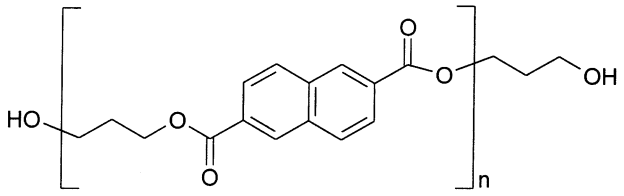

Fig. 1. Structure of PTN.

Huggins constant of PTN in phenol/1,1,2,2-tetrachloroethane was determined to be $k_H = 0.32$ [14].

2.1.2. Carboxyl end groups

The concentration of carboxyl end groups — indicative of thermal degradation — was determined by conductimetric titration with a 0.02N benzyl alcoholic potassium hydroxide solution. For this measurement approximately 4 g of polymer were dissolved in 70 ml of phenol/chloroform (1:1; w/w).

2.1.3. Static light scattering

Static light scattering measurements were performed to determine the weight-average molecular weight M_w. The experiments were carried out in 1,1,1,3,3,3-hexafluoro-2-isopropanol at 20°C using a Sofica apparatus equipped with a HeNe-Laser. The polymer solutions having concentrations between 2 and 10 g/l were filtered through 0.45 μm disposable membrane filters. The intensities of the scattered light were measured over an angular range from 50 to 130° using vertically polarized light (633 nm). The experimental data were analyzed by means of a Zimm plot. A Wyatt Optilab 903 refractometer was used to determine the refractive index increment: $dn/dc = 0.299$ cm^3/g (at 633 nm).

2.1.4. Mark–Houwink–Sakurada equation of PTN

The determination of absolute molecular weights includes a certain experimental error. To minimize this error, we employed the Mark–Houwink–Sakurada (MHS) equation to calculate M_w of the samples in Table 1, where the MHS constants were determined over a wider range of molecular weights. We will use the M_w values in a later section where the effect of molecular weight on the rheological properties is discussed.

By plotting $\ln[\eta]$ vs. $\ln M_w$, the constants K_w and α of the MHS equation could be obtained. This equation reads

$$[\eta] = K_w M_w^{\alpha} \tag{1}$$

Table 1
Relative solution viscosity η_{rel}, intrinsic viscosity $[\eta]$, content of carboxyl end groups COOH, and molecular weight M_w of PTN samples used for the rheological experiments

η_{rel}	$[\eta]$ (dl/g)	*COOH* (μval/g)	M_w (g/mol)
1.68	0.58	< 3	25,800
1.74	0.62	7.5	29,000
1.77	0.64	12.9	30,600
1.87	0.71	18.3	36,600

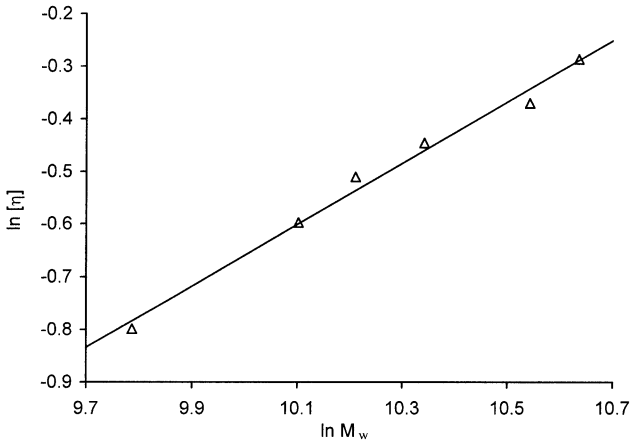

Fig. 2. Mark–Houwink–Sakurada plot of PTN (M_w in g/mol; $[\eta]$ in dl/g).

In Fig. 2 the weight-average molecular weight M_w determined by static light scattering is plotted as a function of the intrinsic viscosity $[\eta]$ for PTN polymers with $[\eta]$ between 0.45 and 0.75 dl/g. According to Fig. 2 the constants α and K_w are found to be

$$\alpha = 0.58; \qquad K_w = 1.55 \times 10^{-3} \text{ dl/g}$$

and thus Eq. (1) becomes

$$[\eta] = 1.55 \times 10^{-3} M_w^{0.58} \tag{2}$$

(valid for $[\eta]$ between 0.45 and 0.75 dl/g)

In this form, the equation is valid only for polymers having the same molecular weight distribution. In its more general form, the MHS equation should be written as

$$[\eta] = K_\eta M_\eta^{\alpha} \tag{3}$$

where M_η is the viscosity-average molecular weight. If we replace M_η in Eq. (3) by the weight-average molecular weight M_w a correction factor q_w has to be introduced which takes the polymolecularity into account [22] and Eq. (3) becomes

$$[\eta] = K_\eta q_w M_w^{\alpha} \tag{4}$$

We assume that the molecular weight distribution of PTN follows Schulz–Flory statistics and thus the correction factor q_w and K_η can be calculated to give

$$q_w(\text{Schulz–Flory}) = \frac{\Gamma(\alpha + 2)}{2^{\alpha}} = 0.942;$$

$$K_\eta = 1.64 \times 10^{-3} \text{ dl/g}$$

where $\Gamma(z)$ represents the gamma function with $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$.

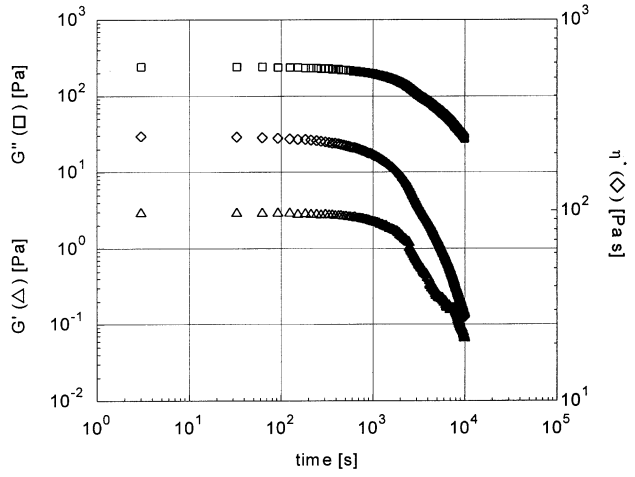

Fig. 3. Storage modulus G', loss modulus G'', and complex viscosity η^* as a function of time for a PTN melt at 270°C ($\omega = 1$ rad/s).

2.2. Rheological measurements

A dynamic stress rheometer (Rheometrics DSR 500) operating in the oscillatory shear mode was used to determine the rheological properties of PTN melts. Measurements were performed with parallel plates of 25 mm diameter, sweeping over a range of frequencies, typically 1.0–500.0 rad/s. To minimize moisture and oxygen pickup during loading and measuring, the rheometer was placed in a glove box under nitrogen. Prior to the measurement, the PTN samples were kept in a vacuum oven for 12 h at 120°C.

After the rheometer plates had reached the desired temperature, an appropriate amount of polyester (approx. 1 g) was placed on the bottom plate and the gap was adjusted to 1.5 mm. It took approximately 10 min before the specimen came to thermal equilibrium and a constant reading of the complex viscosity was obtained.

In order to determine the linear viscoelastic range, the storage modulus, G', and loss modulus, G'', were measured as a function of strain amplitude at constant frequency. The frequency sweep experiments were subsequently carried out with the maximum strain amplitude, where the melt still showed linear viscoelasticity. In the linear viscoelastic range, the complex modulus G^* can be defined as

$$G^* = \frac{\tau^*}{\gamma^*} = \frac{\tau_0\, e^{i(\omega t+\delta)}}{\gamma_0\, e^{i\omega t}} = \frac{\tau_0}{\gamma_0} e^{i\delta} \tag{5}$$

where τ_0 and γ_0 are the amplitudes of shear stress and shear strain, respectively, δ the phase shift between the two, and ω is the oscillation frequency. G^* can be split up into the real and imaginary part

$$G^* = G' + iG'' \tag{6}$$

where G' is the storage modulus and G'' is the loss modulus. Furthermore, the complex viscosity can be defined in the following way:

$$\eta^* = \frac{\tau^*}{\dot\gamma^*} = \frac{G^*}{i\omega} = \frac{G''}{\omega} - i\frac{G'}{\omega} = \eta' - i\cdot\eta'' \tag{7}$$

where the real part of viscosity η^* is related to the loss modulus G'', and the imaginary part to the storage modulus G'. The zero shear viscosity η_0 is obtained when the frequency approaches zero ($\omega \to 0$)

$$\eta_0 = \lim_{\omega\to 0} \frac{G''}{\omega} \tag{8}$$

3. Results and discussion

3.1. Reliability of measured data

As mentioned in Section 1, the stability of polyesters in the melt at high temperatures is limited. Tsai and Lee [12] showed that the melting point of PTN is 204°C. The lowest temperature employed in the rheological investigations was, therefore, 230°C. To estimate the upper limit, some measurements were taken as a function of time at fixed temperature. Fig. 3 gives an example. It shows the storage modulus G', the loss modulus G'', and the complex viscosity η^* as a function of time for a PTN melt at 270°C. G', G'' and η^* are constant over a period of approximately 500 seconds. This time is sufficient for the recording of the rheological data. Despite of the precautions made (inert atmosphere, sample drying, glove box, etc.) we observe a decrease of G', G'', and η^* when the sample is kept for longer periods than approximately 500 s. As the complex viscosity η^* depends strongly on the molecular weight this fact is probably due to the chain degradations discussed before. At lower temperatures than 270°C, the time before degradation is observed is markedly longer.

When the temperature is increased to 280°C, no

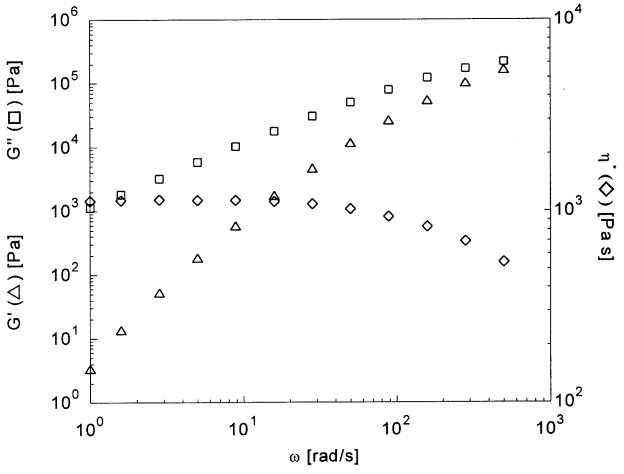

Fig. 4. Log–log plot of the storage modulus G', the loss modulus G'', and the complex viscosity η^* as a function of oscillation frequency ω for a PTN melt at 230°C.

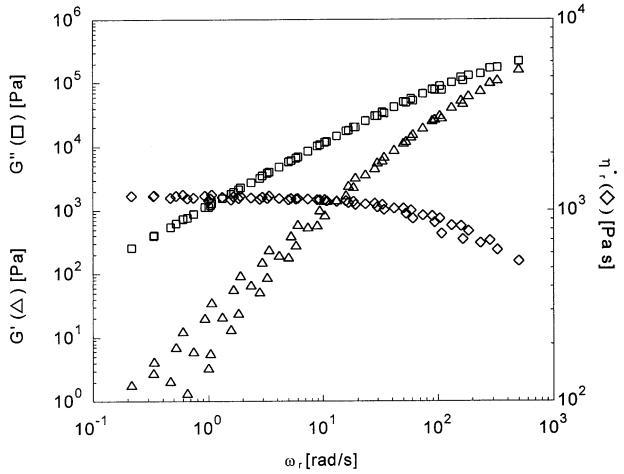

Fig. 5. Master curves for PTN melts between 230 and 270°C using a PTN sample with a molecular weight M_w of 30,600 g/mol (reference temperature $T_0 = 230$°C.

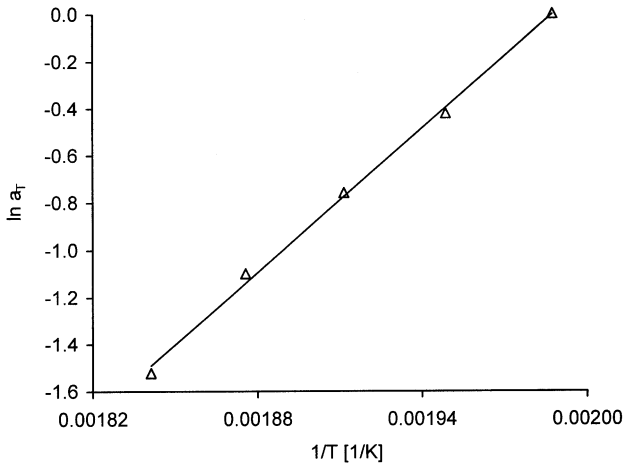

Fig. 6. Arrhenius plot to determine the flow activation energy of PTN.

constancy in G', G'', and η^* is observed and therefore no reproducible data can be obtained. Hence, under the employed experimental conditions, the upper critical temperature to get reliable rheological data on a PTN melt is 270°C.

3.2. Effect of temperature

Rheological measurements were carried out at temperatures between 230 and 270°C using a PTN sample with a molecular weight M_w of 30,600 g/mol. Fig. 4 shows the storage modulus G', the loss modulus G'', and the complex viscosity η^* as a function of oscillation frequency ω at 230°C. Similar data were obtained at 240, 250, 260, and 270°C. With respect to the Cox–Merz rule [23], the viscosity measured in oscillatory shear in the zero-frequency limit equals the low shear viscosity measured in steady shear.

According to the time temperature superposition principle, master curves can be constructed provided that all relaxation times λ_i in the relaxation spectrum have the same temperature dependence. This should be true if there is no phase change or other structural change of the polymer within the temperature range considered. Hence

$$\lambda_i(T) = \lambda_i(T_0)a_T \tag{9}$$

with $a_T < 1$ for $T > T_0$; $a_T = 1$ for $T = T_0$; $a_T > 1$ for $T < T_0$, where a_T is the temperature dependent shift factor, T refers to the actual temperature and T_0 is the reference temperature. Fig. 5 shows such master curves obtained by horizontal shifting to the reference temperature $T_0 = 230$°C. G', G'' and η_r^* are plotted versus the reduced frequency ω_r with $\omega_r = \omega a_T$ and $\eta_r^* = \eta^* / a_T$. The graphical presentation clearly demonstrates that the superposition principle is applicable. The scatter of G' at low frequency is due to the limited accuracy of the rheometer for small G' values at high G''/G' ratio. Table 2 contains a listing of the shift factors a_T and the zero shear viscosities η_0 extrapolated according to Eq. (8).

The temperature dependence of the shift factors a_T can be well described by the Arrhenius relation

$$\ln a_T = \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{10}$$

where R is the universal gas constant and E is the flow activation energy. This is shown in Fig. 6, where $\ln a_T$ is plotted versus $1/T$. The flow activation energy E is found to be 85 kJ/mol. Consequently, the flow behavior of a PTN melt can be calculated for all temperatures within the experimental temperature range considered.

In the literature the flow activation energy of poly(ethylene terephthalate) (PET) was determined to be between 65 and 190 kJ/mol [17–21]. As the melting point of PET with 265°C is much higher than that of PTN, hydrolytic, oxidative, and thermal degradation have a stronger influence during the measurement. Also samples of different molecular weight can explain the significant differences in the flow activation energy of PET.

3.3. Effect of molecular weight

Similar to the temperature dependent shift factor a_T, we can define a molecular weight dependent shift factor a_M.

Table 2
Shift factors a_T and zero shear viscosities η_0 between 230 and 270°C for PTN with a molecular weight M_w of 30,600 g/mol

Temperature (°C)	230	240	250	260	270
Shift factor a_T	1	0.656	0.468	0.333	0.218
Zero shear viscosity η_0 (Pa s)	1134	759	547	395	255

Table 3
Shift factors a_M and zero shear viscosities η_0 for PTN with different molecular weights at 230°C

Relative solution viscosity η_{rel}	1.68	1.74	1.77	1.87
Shift factor a_M	1	1.742	1.897	2.883
Zero shear viscosity η_0 (Pa s)	598	1035	1134	1728
M_w (calculated with a_M) (g/mol)	25,800	30,300	31,100	35,200
M_w (calculated with MHS) (g/mol)	25,800	29,000	30,600	36,600

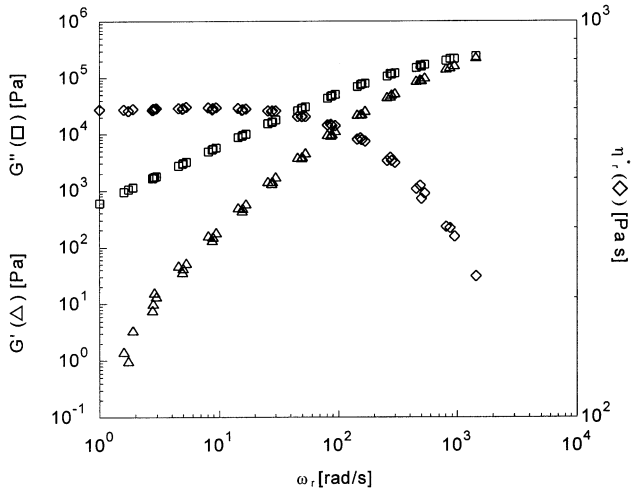

Fig. 7. Master curves for PTN melts with different molecular weights at 230°C.

Above a critical molecular weight, where the macromolecules form a temporary entanglement network, the zero shear viscosity η_0 increases with the molecular weight M according to Eq. (11)

$$\eta_0 = KM_w^{3.4} \tag{11}$$

Hence, the molecular weight dependent shift factor a_M is given by

$$a_M = \left\{ \frac{M_w}{M_{w0}} \right\}^{3.4} \tag{12}$$

We employed the four PTN polymers listed in Table 1 to investigate the effect of molecular weight. The measurements were always carried out at one temperature (230°C). Fig. 7 shows the master curves obtained by applying the appropriate shifting procedure to shift the data to the reference molecular weight M_{w0}, that is 25,800 g/mol. The resulting molecular weight dependent shift factors a_M and the extrapolated zero shear viscosities η_0 are shown in Table 3.

When we define the reference molecular weight M_{w0} to be 25,800 g/mol, we can calculate the other molecular weights M_w using Eq. (12) and the experimentally determined shift factors a_M. The resulting molecular weights M_w are listed in Table 3 (line 4) and are compared with those determined by the MHS equation (line 5, same data as in Table 1). The two sets of data show excellent agreement thus proving the fact that rheological data obtained on polymer melts can be very useful in comparing molecular weights.

4. Conclusions

It has been shown that the temperature dependence of the rheological data of a PTN melt can be expressed by the Arrhenius equation. Furthermore, there is a good agreement between the molecular weights determined: (a) by rheological measurements on melts and (b) by Mark–Houwink–Sakurada equation in combination with light scattering. Thus, a complete set of parameters is now available to calculate the rheological properties of a PTN melt in the temperature range from 230 to 270°C and for molecular weights M_w between 20,000 and 40,000 g/mol.

References

[1] Jakeways R, Ward IM, Wilding MA, Hall IH, Desborough IJ, Pass MG. J Polym Sci Phys Ed 1975;13:799.
[2] Ward IM, Wilding MA, Brody H. J Polym Sci Phys Ed 1976;14:263.
[3] Chuah H. Chem Fibers Int 1996;46:426.
[4] Traub HL, Hirt P, Herlinger H. Chem Fibers Int 1995;45:110.
[5] Oppermann W, Hirt P, Fritz C. Chem Fibers Int 1999;49:14.
[6] Sharma ND, Jain SL. Man-Made Textiles India 1995;38(10):406.
[7] Rim P. Chem Fibers Int 1996;46:204.
[8] Jager J, Juijn JA, van den d. Heuvel CJM, Huijts RA. J Appl Polym Sci 1995;57:1429.
[9] Sadanobu J, Tsukioka M. Annu Tech Conf — Soc Plast Eng 1997;55(2):1567.
[10] Hwang SK, Yeh C, Chen LS, Way TF, Tsay LM, Liu KK, Chen LT. Polym Preprints 1999;40:611.
[11] How C, Forschner T, Lowtan R, Gwyn D, Cristea B. J Plast Film Sheeting 1999;15(3):219.
[12] Tsai RS, Lee YD. J Polym Res 1998;5(2):77.
[13] Stier U, Gähr F, Oppermann W. J Appl Polym Sci 2001;80:2039.
[14] Stier U, Oppermann W. J Polym Sci Polym Chem Ed 2001;39:620.
[15] Zimmermann H, Leibnitz E. Faserforsch Textiltechn 1965;16:282.
[16] Buxbaum LH. Angew Chem 1968;80:225.
[17] Kim BK, Jeong HM, Lee YH. J Appl Polym Sci 1990;40:1805.
[18] Pinaud F. J Non-Newtonian Fluid Mech 1987;23:137.
[19] Park H, Rhim MS. Han'guk Somyu Konghakhoechi 1983;20(5):300.
[20] Schulken RM, Cox RH, Minnick LA. J Appl Polym Sci 1980;25:1341.
[21] Gregory DR. J Appl Polym Sci 1972;16:1479.
[22] Sutter W, Kuppel A. Makromol Chem 1971;149:271.
[23] Cox WP, Merz EH. J Polym Sci 1958;28:619.