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Birefringence in Poly(methyl acrylate) Networks in Elongation[†]

Enrique Saiz*

Departamento de Quimica Fisica, Universidad de Alcala de Henares, Madrid, Spain

Evaristo Riande

Instituto de Plastico y Caucho, Madrid, Spain

James E. Mark

Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221. *Received August 15, 1983*

ABSTRACT: Elastomeric networks were prepared from atactic poly(methyl acrylate) (PMA) chains $[-CH_2CH(COOCH_3)-]_x$, with the required cross-links being introduced by γ-irradiation. They were studied in elongation, both unswollen and swollen with triethylbenzene, with regard to their stress–temperature and birefringence–temperature relationships. At constant length, the stress f/A increases markedly at the glass transition temperature T_g, with values of T_g increasing discernibly with increasing elongation. Values of the birefringence, which were found to be negative, were used to calculate values of the optical configuration parameter Δa and its temperature coefficient. Rotational isomeric state calculations confirm the observation that Δa is negative, with detailed comparisons between theory and experiment giving semiquantitative agreement in the case of Δa and very good agreement for the theoretically more pertinent temperature coefficient of Δa.

Introduction

The birefringence Δn of a polymeric material provides valuable information on the molecular chains from which it is constituted, and this dependence has been much exploited in strain-birefringence studies of elastomeric networks.[1,2] Such studies frequently include measurements over a wide range in temperature, and particularly interesting results may be obtained at temperatures below the glass transition temperature T_g.[2-4] In the vicinity of T_g, both the stress f/A and Δn can change markedly because of intramolecular effects (e.g., distortions of bond angles and stretching of bonds) and changes in intermolecular interactions.[2,3] Such measurements can therefore afford a method for locating T_g and documenting its dependence on network structure and extent of deformation.[5]

Measurements of Δn also provide values of the optical configuration parameter Δa and its temperature coefficient.[6] These quantities are also calculable from rotational isomeric state theory,[6,7] and thus comparisons between experiment and theory can provide valuable information on the spatial configurations of the chains making up the elastomeric network.

The present investigation is concerned with such characterizations of networks prepared from atactic poly(methyl acrylate) (PMA) chains $[-CH_2CH(COOCH_3)-]_x$. The unusual negative birefringence reported for poly(ethyl acrylate) (PEA)[3] focuses particular attention on this additional member of the polyacrylate series.

Experimental Details

A sample of atactic PMA, of viscosity-average molecular weight 1.5×10^6, was molded at 80 °C into a sheet 0.7 mm thick. The sheet was irradiated with a ^{60}Co γ-radiation source, the irradiation dose being 3.6 Mrd. Small strips of cross-sectional area 0.04 cm^2 (at room temperature) were cut from the cross-linked sheet and mounted between clamps, the upper clamp being attached to a force transducer, which could be moved upward so as to impose the desired elongation. The birefringence measurements were made by using a Babinet compensator in the manner described elsewhere.[8,9] The sample was surrounded by a double-walled glass jacket in which an ethylene glycol–water solution was circulated from a thermostat. Temperatures were in the range 0–90 °C and elongations $\alpha = L/L_0$ ranged from 1.1 to 2.5 (where L and L_0 represent, respectively, the deformed and undeformed lengths of the strips). In all cases the strips were stretched at high temperature (ca. 80 °C) and held at this temperature until changes in the force with time were no longer discernible. The network strips were studied both unswollen and swollen with the nonvolatile diluent 1,3,5-triethylbenzene.

Experimental Results

Values of the elastic force f were divided by the cross-sectional area A of the sample strip to give values of the true stress f/A, values of which are shown as a function of temperature in Figure 1. The stress is seen to increase markedly with decreasing temperature in the vicinity of the T_g, ~10 °C, of the high molecular weight un-cross-linked polymer.[10,11] If T_g is taken to be the temperature at which f/A first exhibits discernible departures from linearity, then T_g increases 8 °C over the elongation range studied. The specific values of T_g are 13, 16, 18, 19, and 21 °C for α = 1.103, 1.206, 1.457, 1.906, and 2.519. Since the volume of a typical elastomer increases by a possibly significant few hundredths of a percent when it is stretched,[11] the increase in T_g with increasing α means that the effects of decreasing entropy offset the volume effects.

The birefringence is shown as a function of temperature in Figure 2, with some of the data being compared to the corresponding stress–temperature data in Figure 3. Departures from linearity in the case of Δn generally occur at temperatures above those taken to be T_g on the basis of the stress–temperature curves. Although these temperatures therefore do not identify directly with T_g, it is interesting to note that they also increase significantly with increase in elongation.

As Figures 2 and 3 demonstrate, the birefringence of PMA was found to be negative, as is the birefringence of PEA.[3] For both polymers, the highly polarizable carbonyl groups, perpendicular to the chain axis, are probably responsible for the negative orientation birefringence, which apparently overcomes the positive orientation birefringence of the C–C skeletal bonds.[2,3] Values of the stress-optical coefficient $C = \Delta n/(f/A)$ were obtained by plotting the birefringence against the true stress, as is illustrated in Figure 4. The results are given in column three of Table I. The values of C are, of course, also negative and were found to decrease by a factor of almost one-half as the

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[†] It is a pleasure to dedicate this paper to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

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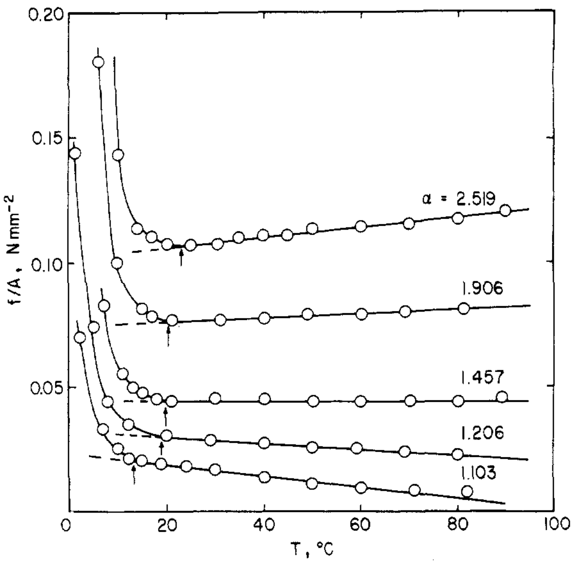

Figure 1. Stress-temperature curves for the poly(methyl acrylate) networks. Each curve is identified with the value of the elongation employed, and the dashed-line extensions help to establish the first departures from linearity (located by the arrows).

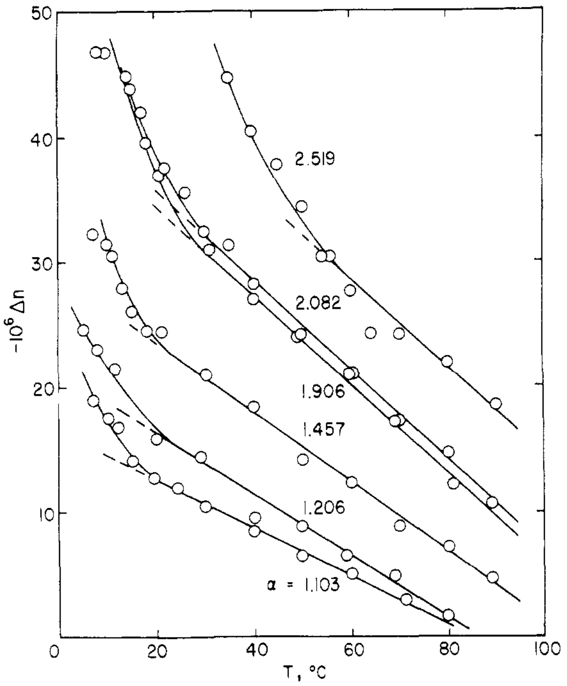

Figure 2. Birefringence-temperature curves for the PMA networks; see legend to Figure 1.

temperature was increased from 50 to 80 °C. Similar behavior has been reported for PEA.[3] Also, as expected,[2,8,9] the values of C for the PMA were significantly decreased by incorporation of the triethylbenzene diluent.

The birefringence results were also used to calculate values of the optical-configuration parameter[6]

$$\Delta a = (45kT/2\pi)[n/(n^2+2)^2][\Delta n/(f/A)] \qquad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, and n is the index of refraction. Because of difficulties in measuring Δn for the swollen networks, values of Δa are presented, in Table I, for only the unswollen network. At 50 °C, the unswollen PMA network gave the results $\Delta a = -0.84 \times 10^{-24}$ cm^3 and $\mathrm{d}\Delta a/\mathrm{d}T = 10.5 \times 10^{-27}$ cm^3 K^{-1}.

Rotational Isomeric State Theory

Structural Information and Statistical Weights.

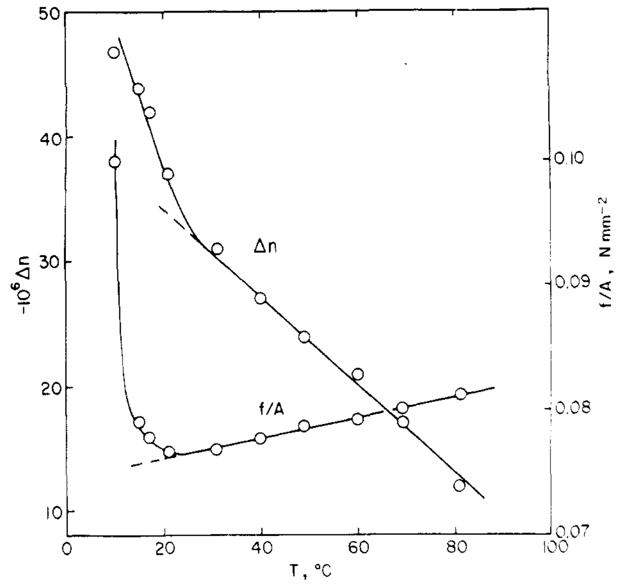

Figure 3. Stress-temperature and birefringence-temperature curves at $\alpha = 1.906$, with the ordinate for the former curve greatly expanded to provide additional detail.

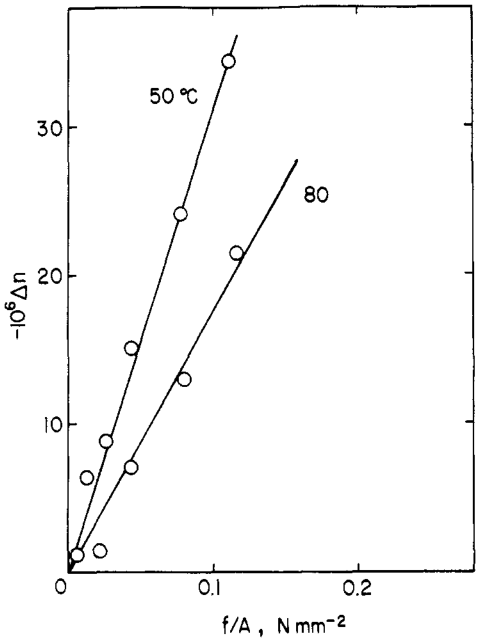

Figure 4. Typical results showing the dependence of the birefringence on the stress, obtained by varying the temperature at constant length. The slope of each curve is the stress-optical coefficient C.

The rotational isomeric state model employed is described in detail elsewhere.[12,13] This simplified two-state scheme is sufficient for calculations of Δa for this polymer, the more elaborate four-state scheme[14,15] being unnecessary. The required structural information was taken from previous investigations.[12-15] Specifically, the C–C skeletal bond length was taken to be 0.153 nm, skeletal bond angles around unsubstituted and substituted C atoms to be 114° and 112°, respectively, and rotational states[7] to be located at dihedral angles of 10° (trans) and 110° (gauche), respectively. The statistical weight matrix for rotations about a pair of bonds leading into a substituted C atom (such as bonds i and $i+1$ of Figure 5) is

$$U' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \qquad (2)$$

Table I
Experimental Values of the Stress-Optical Coefficient and Optical-Configuration Parameter

T, °C	v_2[a]	$-10^{-11}C$, cm^3 dyn^{-1}	$-10^{24}\Delta a$, cm^3
0	0.60	4.06	
10	0.60	3.31	
20	0.60	2.63	
30	0.60	1.79	
40	0.60	1.14	
50	1.00	3.10	0.84
60	1.00	2.60	0.73
70	1.00	2.14	0.62
80	1.00	1.76	0.52

[a] Volume fraction of polymer in the network; for v_2 = 0.60, the diluent was 1,3,5-triethylbenzene.

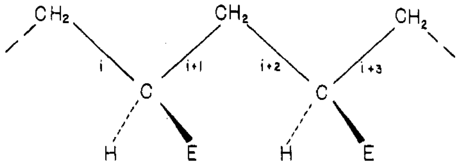

Figure 5. Sketch of the PMA chain, with E representing the $COOCH_3$ group.

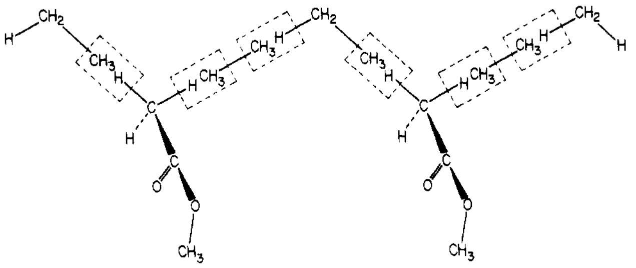

Figure 6. PMA schematically constructed from methyl acetate and ethane in a way that yields information on its polarizability tensor.

The matrices for a pair of bonds separating two substituted C atoms (such as $i + 1$ and $i + 2$) are

$$\mathrm{U_r}'' = \begin{bmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{bmatrix} \tag{3a}$$

$$\mathrm{U_m}'' = \begin{bmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{bmatrix} \tag{3b}$$

for racemic (syndiotactic) and meso (isotactic) placements, respectively. The statistical weights are given by [13] ω' = 1.4 exp($-1600/RT$), η = exp($300/RT$), ω'' = 1.2 exp($-1500/RT$), and ω = 1.3 exp($-1600/RT$) when the gas constant R is in cal deg^{-1} mol^{-1}.

Anisotropic Part of the Polarizability Tensor. The polarizability tensor $\hat{\alpha}$ for the PMA chain may be obtained by addition of contributions associated with each skeletal bond. In order to formulate these contributions, one utilizes the fact that the PMA chain can be formally obtained from molecules of methyl acetate (MA) and ethane (ET) with removal of one and two molecules of methane for each CH_2–C and C–CH_2 skeletal bond, respectively. This is illustrated in Figure 6. Since the methane molecule has spherical symmetry, the anisotropic part of its polarizability tensor is null, and, therefore, the tensor for CH_2–C bonds such as bond i in Figure 5 is simply

$$\hat{\alpha}_i = \hat{\alpha}_{\mathrm{ET}} = \hat{\alpha}_{\mathrm{CC}} - 2\hat{\alpha}_{\mathrm{CH}} \tag{4}$$

This tensor is also given by[16]

$$\hat{\alpha}_i = \Gamma_{\mathrm{CC}}\ \mathrm{diag}\ (\tfrac{2}{3}, -\tfrac{1}{3}, -\tfrac{1}{3}) \tag{5}$$

Table II
Calculated Values of the Optical-Configuration Parameter and Its Temperature Coefficient at 50 °C

P_r	$-10^{24}\Delta a$, cm^3	$10^{27}(\mathrm{d}\Delta a/\mathrm{d}T)$, cm^3 K^{-1}
0.0	13.2	23.8
0.5	5.44 (±0.18)	8.94
1.0	4.92	9.05

with $\Gamma_{\mathrm{CC}} = 0.53 \times 10^{-24}$ cm^3 in a coordinate system that has the x axis along the C–C bond and that coincides with the reference frame associated with skeletal bond i. The tensor for C–CH_2 bonds (such as $i + 1$) is

$$\hat{\alpha}_{i+1} = \hat{\alpha}_{\mathrm{ET}} + (\hat{\alpha}_{\mathrm{MA}}) \tag{6}$$

where the parentheses indicate that the α_{MA} tensor has to be transformed into the reference frame associated with skeletal bond $i + 1$ before the addition may be performed. The tensor for a methyl acrylate molecule in a coordinate system having the x axis along the CH_3–C bond and the y axis in the plane of the molecule is[17]

$$\hat{\alpha}_{\mathrm{MA}} = \begin{bmatrix} 1.03 & -0.1 & 0 \\ -0.1 & 0.09 & 0 \\ 0 & 0 & -1.12 \end{bmatrix} =$$

$$\begin{bmatrix} \alpha_x & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_y & 0 \\ 0 & 0 & \alpha_z \end{bmatrix} = \begin{bmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} +$$

$$\Delta\alpha\ \mathrm{diag}\ (2/3, -1/3, -1/3) + \Delta\alpha^{+}\ \mathrm{diag}\ (0, 1/2, -1/2) \tag{7}$$

with $\Delta\alpha = 1.545$ and $\Delta\alpha^{+} = 1.21 \times 10^{-24}$ cm^3. The calculated values of Δa depend only slightly on α_{xy}, since its magnitude is only 0.1×10^{-24} cm^3, with side-group rotation from cis to trans affecting only its sign. Averaging over cis and trans orientations of the ester group requires establishing the effect of a 180° rotation about the C–CH_2 bond on the $\hat{\alpha}$ tensor. The result of the required transformations[18] is then used in the averaging, with the cis orientation preferred over the trans by approximately 200 cal mol^{-1}.[13,19] The averaged tensor thus obtained is

$$\hat{\alpha}_{i+1} = \begin{bmatrix} -0.2610 & -0.7497 & 0.2602 \\ -0.7497 & -0.1852 & -0.3864 \\ 0.2606 & -0.3864 & 0.4462 \end{bmatrix}$$

Numerical Calculations. Stereochemical structure was characterized by the replication probability P_r, with values of 0.0, 0.5, and 1.0 corresponding to syndiotactic, atactic, and isotactic chains, respectively. For values of $0 < P_r < 1$ (stereochemical irregularity), Monte Carlo simulations with Bernoullian placements were used to generate ten representative chains at each desired value of P_r. The standard methods of matrix multiplication[7,20] were then used to calculate values of Δa for different degrees of polymerization x over the temperature range of interest.

Calculated Results and Discussion

The values of Δa at 50 °C calculated for the illustrative values P_r = 0.0, 0.5, and 1.0 are shown as a function of the degree of polymerization x in Figure 7. As can be seen, Δa is already very close to its value in the limit of very high chain length at x = 100. These limiting values and their temperature dependence are presented in Table II. The results of more extensive calculations on the effect of stereochemical structure are shown in Figure 8. The stress-optical coefficient is seen to be most sensitive to P_r in the syndiotactic region.

For the atactic polymer, the calculated value of Δa is -5.4×10^{-24} cm^3 at 50 °C, which is in only semiquantitative

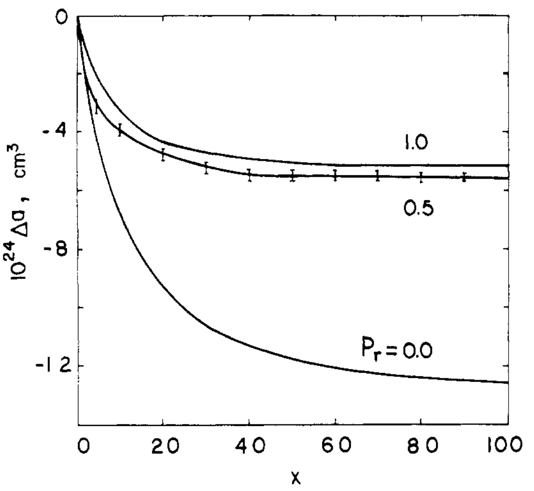

Figure 7. Calculated dependence of the optical-configuration parameter on the degree of polymerization for illustrative values of the replication probability, which characterizes the stereochemical structure of the chains.

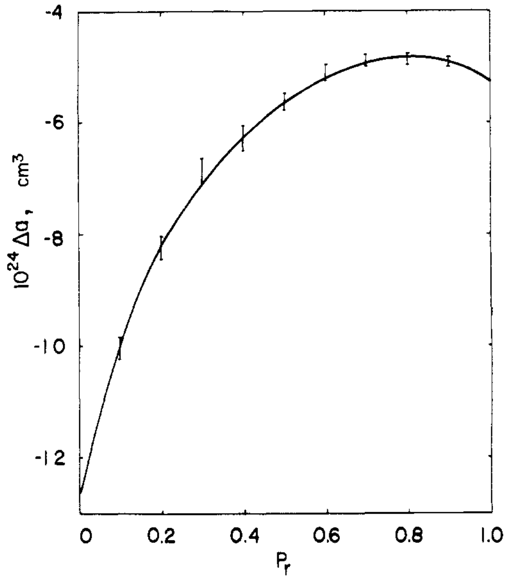

Figure 8. Calculated dependence of the optical-configuration parameter on the stereochemical structure of the chains in the limit of large chain length.

agreement with the experimental value -0.84×10^{-24} cm^3, presumably because of difficulties in formulating sufficiently accurate polarizability tensors. Additional calculations of $\Delta\alpha$ were carried out for different values of $\Delta\alpha$, $\Delta\alpha^+$, and the various statistical weights. The agreement between theory and experiment would not be greatly improved with reasonable changes in these parameters. The calculated value of the temperature coefficient $d\Delta\alpha/dT$ was found to be 8.94×10^{-27} cm^3 K^{-1}, which is very close to the experimental value 10.5×10^{-27} cm^3 K^{-1}. The latter very good agreement is particularly gratifying since $d\Delta\alpha/dT$ is virtually independent of the ansiotropic part of the group polarizability tensor required in the rotational isomeric state calculations. It is thus much more pertinent than $\Delta\alpha$ itself[6,21] with regard to characterizing the spatial configurations of the network chains.

The agreement between theoretical and experimental values of $\Delta\alpha$ for most other polymer chains has similarly been found to be only approximate. It is gratifying to note, however, that the calculations do reproduce the rather unusual negative birefringence of PMA. Its origin was elucidated in the present calculations. In the case of symmetrical chains made up of bonds of low polarizability, such as polyethylene, the largest component of the polarizability tensor is positive and lies along the C–C skeletal bond (x axis); as a consequence, the optical-configuration parameter will be positive. However, when a strongly anisotropic group is present as a side chain, as occurs in PMA, large negative components α_{xx} and α_{xy} may appear in the tensor. These give rise to negative contributions to the quantity $\mathbf{r}^T\hat{\alpha}\mathbf{r}$[6,21] (where $\mathbf{r}^T$ is the transpose of the end-to-end vector $\mathbf{r}$) which appears in the theoretical expression for $\Delta\alpha$, and these can overcome contributions from the positive components α_{xz} and α_{zz}.

The calculations suggest that the value of $\Delta\alpha$ is strongly dependent on the syndiotactic content of the chain. The reason is that for syndiotactic placements the most stable conformation is the planar zigzag (all trans), and although the α_{zz} component of the tensor contributes positively to $\mathbf{r}^T\hat{\alpha}\mathbf{r}$, that contribution is much smaller than the negative contributions corresponding to the α_{xx} and α_{xy} components of the tensor which are combined with the large value of r_x (associated with α_{xx} and α_{xy} in the product $\mathbf{r}^T\hat{\alpha}\mathbf{r}$). For isotactic chains, on the contrary, the most stable conformation is ...tgtgtg..., occasionally separated by tt conformations; here, r_x is smaller than in ...tttt... conformations and, as consequence, the contributions of the α_{xx} and α_{xy} components to $\mathbf{r}^T\hat{\alpha}\mathbf{r}$ is less pronounced than in the case of the syndiotactic chains.

Finally, increasing the temperature decreases the value of r_x and for this reason the value of $d\Delta\alpha/dT$ should be positive, and this is confirmed by the experimental results.

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Registry No. Poly(methyl acrylate) (homopolymer), 9003-21-8.

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